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LABORATORY INVESTIGATIONS IN SUPPORT OF FLUID BED FLUORIDE VOLATILITY PROCESSES

Part II. The Properties of Plutonium Hexafluoride

by

Martin J. Steindler

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LABORATORY INVESTIGATIONS IN SUPPORT OF
FLUID BED FLUORIDE VOLATILITY PROCESSES

PART II. THE PROPERTIES OF PLUTONIUM HEXAFLUORIDE

by

Martin J. Steindler

Chemical Engineering Division

August 1963

Part I of this series is ANL-6742
Part III of this series is ANL-6762
Part IV of this series is ANL-6763

Operated by The University of Chicago
under
Contract W-31-109-eng-38
with the
U. S. Atomic Energy Commission

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ABSTRACT

All of the properties of plutonium hexafluoride reported up to May 1963 are summarized, and pertinent data are presented in detail. Included are the preparation of plutonium hexafluoride, physical properties, absorption spectra, chemical reactions, decomposition of plutonium hexafluoride by radiation and heat, the corrosion of materials of construction by plutonium hexafluoride, and a summary of the biological and radiological hazards from plutonium hexafluoride. An appendix containing an expanded vapor pressure table is included.

1.0 INTRODUCTION

Plutonium hexafluoride is the only stable compound of plutonium which is volatile at low temperatures and hence may be separated from uranium and from fission products by distillation. Early work on plutonium hexafluoride was carried out with very small samples; only when large quantities of plutonium became available was the study of plutonium hexafluoride expanded to include the determination of many physical properties.

At this time, data on plutonium hexafluoride are scattered throughout a large number of reports that are often difficult to obtain. In view of this, all of the available data on plutonium hexafluoride have been collected in one reference. Wherever possible, pertinent data are reproduced from the cited literature in the hope that this will eliminate the necessity of seeking the original references. Evaluation of conflicting data is made in some instances to gain a larger measure of coherence.

2.0 HISTORICAL

Early experiments, specifically designed to produce a fluoride of plutonium analogous to uranium hexafluoride, yielded contradictory results. The suggestion that uranium could be separated from plutonium by fluorination of uranium was published as early as June 1942.⁽¹⁾ Experiments carried out at that time with very small quantities of plutonium showed that volatilization of plutonium in a stream of fluorine occurred only above 700 C. Later experiments⁽²⁾ showed that plutonium could be volatilized from a copper dish at 500 C by fluorine and that the rate of volatilization in fluorine decreased from uranium to neptunium and plutonium. Brown and Hill,⁽³⁾ using microgram quantities of plutonium mixed with uranium hexafluoride, concluded from a series of distillation experiments that the higher fluoride of plutonium was unstable in the absence of fluorine and decomposed to plutonium tetrafluoride at room temperature. Davidson, Katz, and Orlemann⁽⁴⁾ volatilized plutonium in an atmosphere of fluorine from nickel filaments onto a cold surface, but failed to redistill the plutonium even when the condensing surface was heated to 200 C. Fischer, Voslow, and Tevebaugh⁽⁵⁾ concluded that the higher fluoride of plutonium has a negative heat of formation and is stable only at elevated temperatures in an atmosphere of fluorine. Florin⁽⁶⁾ prepared a volatile fluoride of plutonium which he condensed onto a glass surface. However, the material proved too reactive to identify. On the basis of the relationship between uranium and plutonium compounds, Brewer⁽⁷⁾ predicted the properties of plutonium hexafluoride and indicated that all lower fluorides could be oxidized to plutonium hexafluoride at reasonable temperatures.

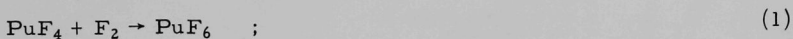
No further work on plutonium hexafluoride was reported until 1950, when A. E. Florin at Los Alamos prepared relatively large amounts of the hexafluoride.⁽⁸⁾ Subsequent to the work of Florin,⁽⁹⁾ other groups became interested in plutonium hexafluoride. Of particular note are the contributions made by B. Weinstock and coworkers at Argonne National Laboratory. The considerable current literature on plutonium hexafluoride indicates the growth of interest in this compound.

3.0 PREPARATION, PURIFICATION, HANDLING, AND STORAGE OF PLUTONIUM HEXAFLUORIDE

3.1 Preparation of Plutonium Hexafluoride

3.1.1 Reactions Using Elemental Fluorine

Plutonium hexafluoride is most easily prepared by using elemental fluorine as the oxidizing-fluorinating agent and, indeed, this reagent is the only one which has produced unequivocal results in preparative experiments. The stoichiometry of preparative reactions varies with the starting material. Two of the most common reactions are shown in Equations 1 and 2:



The fluorination of plutonium dioxide produces oxygen which accumulates in apparatus in which the gases are recirculated over the unreacted solid, and periodic removal of oxygen is required to avoid dilution of fluorine. Moreover, since the fluorination of plutonium dioxide proceeds through the tetrafluoride as an intermediate, the preferred method of preparing of plutonium hexafluoride is the fluorination of plutonium tetrafluoride.

3.1.1.1 Kinetics of the Formation of Plutonium Hexafluoride

The rate of formation of plutonium hexafluoride by fluorination of the dioxide and the tetrafluoride has been studied by Steindler *et al.*(11) The reactions were carried out in small, hemicylindrical, nickel boats, and the course of the reaction was followed by observing the weight change of the contents of the boat. Measurable rates of reaction were observed at temperatures as low as 200 C. The absolute rate of fluorination of plutonium tetrafluoride was shown to be dependent on the history of the sample. For example, plutonium tetrafluoride obtained by the dissolution of uranium-plutonium alloys in bromine trifluoride at room temperature reacted more rapidly than samples of the tetrafluoride obtained by the hydrofluorination of plutonium dioxide at elevated temperatures.

When the logarithms of the reaction rates, expressed in terms of mg PuF_4 reacted per hr per cm^2 of surface area of the sample, were plotted against the reciprocal of the absolute temperature in the usual Arrhenius plot, shown in Figure 1, the resulting straight lines yielded activation energies of between 10.4 and 12.5 kcal/mole.

The larger activation energies were obtained from samples prepared at elevated temperatures, which therefore had smaller specific surface areas. The rate of reaction of plutonium tetrafluoride prepared at elevated temperatures by use of hydrogen fluoride and having a bulk density of 1.3 g/cm^3 is given by the expression

$$\log_{10} \text{ rate (mg PuF}_4 \text{ hr}^{-1} \text{ cm}^{-2}) = 5.917 - (2719/T) \quad ,$$

where T is temperature on the Kelvin scale. At flow rates of fluorine above a minimum, the rate of reaction appears to be independent of fluorine flow rate.

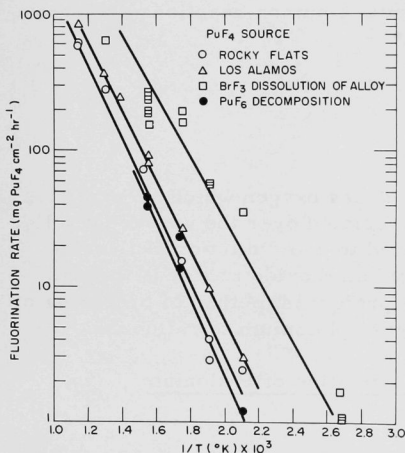


Figure 1
TEMPERATURE DEPENDENCE OF
FLUORINATION RATES OF PLU-
TONIUM TETRAFLUORIDE⁽¹¹⁾

108-2910

The rate of fluorination of plutonium tetrafluoride by mixtures of fluorine and helium or of fluorine and oxygen⁽¹¹⁾ showed a relatively complicated dependence on fluorine concentration. The rate of reaction reached a maximum at a partial pressure of fluorine of 0.75 atm in both types of experiments, but the maximum in the rate becomes less pronounced as the temperature is increased. Figure 2 illustrates this effect. A small amount of an oxygen-containing compound, presumed to be plutonium dioxide, was observed in the residual solid when the fluorination was carried out with fluorine-oxygen mixtures.

Mandleberg and coworkers⁽¹²⁾ also studied the fluorination of plutonium tetrafluoride, but concluded that the reaction rate is not measurable below 320 C. Further, they indicated that the reaction rate of plutonium trifluoride and fluorine to form plutonium hexafluoride is approximately one-half that of the tetrafluoride with fluorine. Since the trifluoride is rapidly converted to plutonium tetrafluoride at room temperature,⁽¹⁵⁾ this relation between the relative rates does not appear likely.

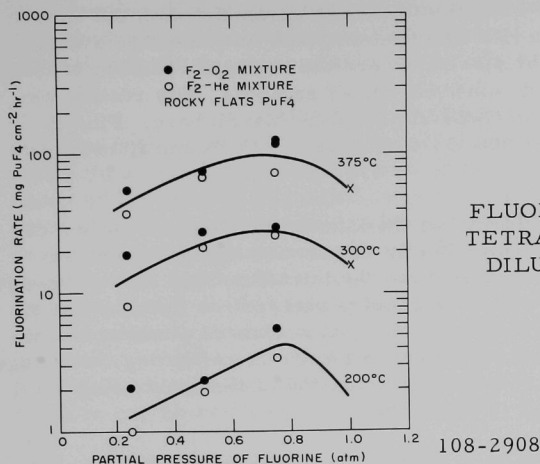


Figure 2
FLUORINATION OF PLUTONIUM
TETRAFLUORIDE BY FLUORINE
DILUTED WITH HELIUM AND
WITH OXYGEN⁽¹¹⁾

Gendre⁽¹³⁾ also studied the rate of fluorination of plutonium tetrafluoride and fitted the data to the diminishing-sphere approximation for gas-solid reactions in a fashion similar to that reported by Steindler and Steunenber.⁽¹⁴⁾ The results obtained by Gendre, when plotted on an Arrhenius plot, show a break in the curve at approximately 370 C, interpreted as being caused by a change in the nature of the solid phase being fluorinated (see Section 5.1.11). The two values for the activation energy obtained by Gendre are 10.5 kcal/mole at 200 to 370 C and 8.6 kcal/mole above 370 C. Gendre also studied briefly the effect of fluorine concentration on the rate of fluorination of plutonium tetrafluoride and observed an increase in the rate of reaction with increasing fluorine concentration. Owing to the fact that Gendre carried out the fluorinations at elevated temperatures (510 C), a maximum in the rate of fluorination at a fluorine partial pressure of 0.75 atm was not observed; rather, a reduction in the effect of increasing fluorine concentration above 0.75 atm is reported. These results are in agreement with those reported by Steindler⁽¹¹⁾ who observed a decreasing effect of the partial pressure of fluorine on the rate of reaction as the reaction temperature is increased. Gendre also reported some results on the effect of surface area, thickness of sample, and duration of reaction on the rate of reaction of plutonium tetrafluoride and fluorine.

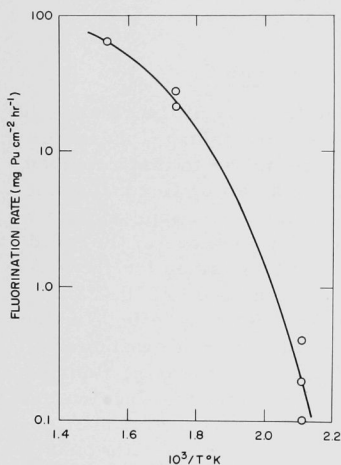
Steindler⁽¹¹⁰⁾ studied the fluorination of mixtures of plutonium tetrafluoride and uranium tetrafluoride by elemental fluorine. The results indicated that the major portion of the uranium is converted to the hexafluoride before plutonium hexafluoride is formed. These results are interpreted as being due to the reaction of plutonium hexafluoride and uranium tetrafluoride to form uranium hexafluoride (see Section 5.1.12).

Other investigators have commented on the rate of reaction of plutonium tetrafluoride and fluorine, but no quantitative data are available. Florin^(9c,10) briefly examined the rates of reaction of PuF_4 and fluorine at 700 C, but used relatively small samples. His results obtained were slightly higher than those reported by Mandleberg. Finally, Weinstock⁽¹⁵⁾ indicated that at 800 C the reaction of PuF_4 and fluorine is "very rapid."

Experiments on the kinetics of the fluorination of plutonium dioxide⁽¹¹⁾ were complicated by the partial conversion of the dioxide to the tetrafluoride. As anticipated, the Arrhenius plot for the fluorination of plutonium dioxide showed a curvature, illustrated in Figure 3, reflecting the change in the composition of the solid being fluorinated.

Figure 3

TEMPERATURE DEPENDENCE OF PLUTONIUM DIOXIDE FLUORINATION RATES⁽¹¹⁾



108-3102

3.1.1.2 Fluorination of $\text{PuO}_2\text{-UO}_2$ Solid Solutions

An extensive investigation of the fluorination of solid solutions of plutonium dioxide and uranium dioxide has been carried out by Fischer and Jarry.⁽¹⁶⁻²¹⁾ These investigators studied the conversion of the oxides to a mixture of hexafluorides under various conditions related to the development of processes using fluid-bed reactors for the recovery of spent nuclear reactor fuels. In the presence of Alundum as an inert fluid-bed material, these workers demonstrated quantitative removal of plutonium from the Alundum by fluorine at 550 C when this reaction was preceded by the removal of uranium as the hexafluoride at 450 C by use of dilute fluorine. The presence of nonvolatile fission products in the mixture did not impair the removal of plutonium if the sample was oxidized with elemental oxygen prior to fluorination.

3.1.1.3 Fluorination of the Decomposition Product of Plutonium Hexafluoride

The fluorination of the solid produced by decomposition of plutonium hexafluoride has been studied by several groups. Fischer⁽²²⁾ reported on the fluorination of plutonium tetrafluoride formed in a nickel vessel by the thermal decomposition of plutonium hexafluoride.

Fluorination of a 30-g sample of the tetrafluoride at 450 C resulted in a 98% recovery of the plutonium as plutonium hexafluoride. Adams et al.⁽²⁴⁾ showed that the decomposition product can be fluorinated at 250 C.

Robb⁽²³⁾ investigated the removal of plutonium deposits from type 75ST6 aluminum by low-temperature fluorination techniques. Robb found that measurable rates of fluorination of a plutonium compound originally deposited by reduction of the hexafluoride by aluminum were observed at temperatures as low as 170 C. The heat of reaction observed by Robb agreed roughly with the heat for the reaction of plutonium tetrafluoride and fluorine, indicating that plutonium tetrafluoride is the solid deposited on the metal samples. These data, together with the observations made by Steindler et al.⁽¹¹⁾ on the kinetics of the fluorination of plutonium tetrafluoride obtained by the thermal decomposition of the hexafluoride, indicate that plutonium deposited by decomposition of the hexafluoride can be recovered quantitatively at relatively low temperatures.

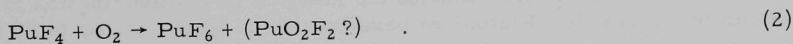
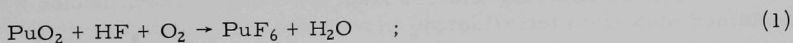
3.1.2 Preparations Using Fluorinating Agents Other than Fluorine

3.1.2.1 Chlorine Trifluoride

As part of the early work on the fluorination of plutonium compounds, Steindler and Vogler⁽²⁵⁾ showed that gaseous chlorine trifluoride at 250 to 400 C can be used to volatilize plutonium plated on nickel coupons. The rate of loss of plutonium from use chlorine trifluoride at 400 C was greater than with fluorine at the same temperature. No further results on the use of this reagent have been reported in the literature.

3.1.2.2 Miscellaneous

Mandleberg⁽¹²⁾ has mentioned several reactions designed to yield plutonium hexafluoride without the use of fluorine, such as



Reaction 1 is based on the observation⁽²⁶⁾ that plutonium was volatilized in a stream of HF-O₂. No identification of the product is given. The reaction analogous to (2) has been shown to produce uranium hexafluoride and uranyl fluoride,⁽¹¹²⁾ but Hawkins⁽²⁷⁾ has shown that the reaction of PuF₄ and O₂ at 800 to 950 C does not produce PuF₆, but a solid of low volatility, possibly Pu₄F₁₇, observed on the colder portions of the equipment. It is necessary to conclude at this time that no reaction designed

to produce plutonium hexafluoride without the use of elemental fluorine has been adequately demonstrated.

Spedding and Newton⁽¹⁰⁶⁾ indicated that uranium may be separated from plutonium by first fluorinating uranium with elemental fluorine at 315 C and subsequently raising the temperature to 500 C to form plutonium hexafluoride. Brown and Webster⁽¹⁰⁷⁾ separated the hexafluorides of uranium and plutonium, formed at 250 C, by distillation. Owing to the small quantities of plutonium available to these authors, the reliability of their results is subject to question.

Malm⁽¹⁰⁸⁾ separated fission products from plutonium by forming platinum hexafluoride at 900 to 1100 C from the elements and subsequently contacting the hexafluoride with the plutonium-containing mixture at room temperature. The latter reaction forms plutonium hexafluoride which is distilled off.

3.1.2.3 Gamma Radiation

Steindler and Steidl⁽²⁸⁾ studied the effect of gamma radiation on the system plutonium tetrafluoride-fluorine in the course of experiments on the decomposition of plutonium hexafluoride by gamma radiation. It was possible to show that irradiation of mixtures of plutonium tetrafluoride and fluorine produced plutonium hexafluoride at concentrations greater than would be calculated from the thermodynamic data on the equilibrium for the system plutonium hexafluoride-plutonium tetrafluoride-fluorine. The product was identified as plutonium hexafluoride by its vapor pressure and the infrared spectrum.

3.1.3 Apparatus for Preparative Reactions

Owing to the high temperatures which were believed to be necessary for the preparation of plutonium hexafluoride, both Florin⁽⁸⁻¹⁰⁾ and Weinstock⁽¹⁵⁾ used induction heating to raise the temperature of samples of plutonium tetrafluoride. Figure 4 shows a typical fluorination reactor. Mandleberg and coworkers⁽¹²⁾ used a tube furnace which contained plutonium tetrafluoride in a nickel boat. Steindler et al.⁽¹¹⁾ used a tube furnace in the study of the kinetics of the fluorination of plutonium tetrafluoride. Plutonium hexafluoride in quantities up to 80 g have been prepared by use of tube furnace reactors.

Optimum yields in the preparation are usually obtained by rapid quenching of the reaction products. In equipment which used induction heating of a vessel containing the starting material (PuF_4), cooling of the induction coil by liquid nitrogen has been successful in rapidly condensing the product. Cold-finger condensers located close to the heated zone have also been used with good results (see Figure 5).

In apparatus using a heated tube containing a boat, fluorine is passed over the sample of plutonium tetrafluoride or the dioxide, and the gas mixture containing plutonium hexafluoride is swept out of the heated zone into a cold trap in which the plutonium hexafluoride condenses. Although it is possible to achieve complete conversion of plutonium tetrafluoride (or oxide) to the hexafluoride, the yields are normally not 100 percent, since some thermal decomposition to the tetrafluoride is usually encountered, particularly in that portion of the equipment which is at temperatures intermediate between the cold trap and the heated reaction zone.

Figure 4

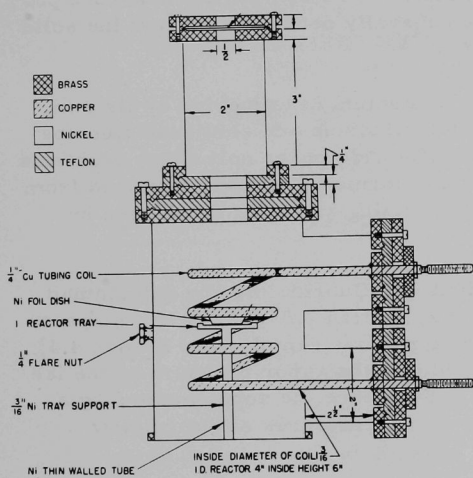
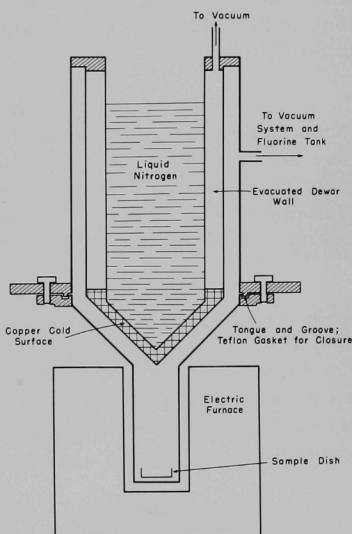
FLUORINATION REACTOR⁽¹⁰⁾

Figure 5

FLUORINATION REACTOR⁽²⁹⁾

120-1582

3.2 Purification, Handling, and Storage of Plutonium Hexafluoride

3.2.1 Purification

Plutonium hexafluoride prepared from the tetrafluoride and elemental fluorine normally requires purification prior to use in careful experiments. Contaminants that are likely to be encountered are those found in elemental fluorine (CF_4 , SiF_4 , CO_2), hydrogen fluoride from the hydrolysis of plutonium hexafluoride by traces of moisture, and the reaction products of plutonium hexafluoride with materials of construction. These impurities may be separated from plutonium hexafluoride by trap to

trap distillation with plutonium hexafluoride being condensed at -80°C .^(15,30) Another method of purification consists of holding the sample of plutonium hexafluoride at -80°C while pumping on the sample under a good vacuum.

Large samples of impure plutonium hexafluoride are somewhat difficult to purify, presumably because of inclusions of impurities in the condensing solid. In this instance, trap to trap distillation, preferably with small portions of the sample, is effective. If plutonium hexafluoride is adsorbed on plutonium tetrafluoride, removal of plutonium hexafluoride by vacuum transfer at room temperature cannot be efficiently achieved. This is particularly true in the case of adsorption on finely divided plutonium tetrafluoride, such as that produced in the decomposition of plutonium hexafluoride by its own alpha radiation.⁽³¹⁾ To remove the adsorbed plutonium hexafluoride efficiently it is generally necessary to heat the solid to 60°C .

The decomposition of plutonium hexafluoride by its own alpha radiation produces plutonium tetrafluoride and elemental fluorine (see Section 5.4). The plutonium tetrafluoride poses only those problems mentioned above. The fluorine which is formed is readily removed from plutonium hexafluoride by repeated warming and cooling followed by evacuation of the gaseous fluorine.

The purity of plutonium hexafluoride may be determined from its vapor pressure (see Appendix, Section 7.0) at a known temperature and by the infrared spectrum of a gaseous sample (see Section 4.4). For high accuracy, it is recommended that the vapor pressure at the ice point, normally used because of its convenience, be supplemented by a determination of the vapor pressure at temperatures slightly below ambient.

3.2.2 Handling

Plutonium hexafluoride can be handled in equipment constructed of quartz and of certain plastics and metals without loss by chemical reaction, provided that these materials are carefully treated to remove all traces of moisture and other impurities.⁽¹⁵⁾ Metal equipment should be carefully assembled to be completely free of leaks and free of grease, solder flux, and other impurities. Prefluorination of equipment with elemental fluorine or similar strong fluorinating agents is usually necessary.⁽²⁴⁾ Pretreatment with plutonium hexafluoride reduces the loss of hexafluoride on equipment walls but does cause deposition of plutonium tetrafluoride. Although high vacuum is not required for successful manipulation, availability of a high-vacuum system is most desirable, and little work is reported in the literature in which a high-vacuum system was not employed. The most commonly used materials of construction include nickel, Monel, and quartz. Copper has been used but may be

more reactive than nickel or Monel. Teflon and Kel-F appear to be satisfactory at room temperature, but only Teflon appears satisfactory at higher temperatures. Plutonium hexafluoride appears to dissolve slowly in Kel-F at room temperature.^(8,15)

Table 1 illustrates the data of Fischer,^(32,33) who has shown that plutonium hexafluoride can be transferred quantitatively in laboratory equipment, but only if care is exercised in the maintenance of a clean, pretreated system. Small quantities of moisture adsorbed on the walls of equipment will lead to losses of plutonium hexafluoride and the generation of hydrogen fluoride.

Table 1

RECOVERIES OBTAINED WHEN TRANSFERRING PLUTONIUM HEXAFLUORIDE

Temperature of transfer path: 70 C

PuF ₆ Vaporized, g	PuF ₆ Recovered in Condenser, g	Recovery, %	Transfer Gas
28.43 (0.04) ^a	28.40 (0.05) ^a	99.98	He
28.49 (0.04)	28.35 (0.01)	99.51	He
23.38 (0.05)	23.37 (0.08)	99.96	He
48.82 (0.05)	48.53 (0.00)	99.41	He
46.07 (0.02)	45.83 (0.01)	99.48	He
40.49 (0.03)	40.21 (0.01)	99.31	He
14.90 (0.08)	14.93 (0.43)	100.20	F ₂
44.80 (0.06)	44.81 (0.00)	100.02	(Vacuum)

^aSmall corrections were made for loss of fluorine by alpha-radiation decomposition. The correction, in grams, is shown in parentheses.

Berard⁽³⁴⁾ reports various aspects of handling of plutonium hexafluoride and discusses the deposition of plutonium hexafluoride on walls of vessels under several conditions.

Plutonium hexafluoride is highly toxic, and work with plutonium requires precautions, which are more fully described in Section 6.0.

3.2.3 Storage of Plutonium Hexafluoride

Plutonium hexafluoride shows little or no thermal decomposition at ambient laboratory temperatures and, hence, may be stored under

these conditions. The material of construction of storage containers must be unreactive toward the hexafluoride; the materials mentioned in the preceding section are satisfactory.

The decomposition of plutonium hexafluoride by its own alpha radiation will, at low temperatures, be the major cause of loss of plutonium hexafluoride. The rate of decomposition of plutonium hexafluoride by alpha radiation is considerably greater in the solid than in the gas phase (see Section 5.4); hence, storage of plutonium hexafluoride in the gas phase is preferable if prohibitively large volumes are not required because of sample size and the low vapor pressure of plutonium hexafluoride at ambient laboratory temperatures. Samples of plutonium stored in the solid should be freed periodically from accumulated fluorine.

Hawkins⁽³⁵⁾ has suggested a method of storage of plutonium hexafluoride in which the hexafluoride is dissolved in a volatile fluorocarbon, such as carbon tetrafluoride, and the solution maintained at a very low temperature. No experimental results were cited by Hawkins. Although this method may be of value in some special cases, it is unlikely that general use of the method is warranted.

4.0 PHYSICAL PROPERTIES

4.1 Phase Relations

4.1.1 Melting Point

The melting point of plutonium hexafluoride has been determined by Weinstock⁽¹⁵⁾ as 50.75 ± 0.1 C. Mandleberg⁽¹²⁾ also determined the melting point of plutonium hexafluoride but found a value of 54 ± 1 C. Florin⁽¹⁰⁾ calculated the triple point from the intersection of the vapor pressure curves for the solid and the liquid, and obtained a value of 50.7 C. Weinstock,⁽³⁶⁾ using the same technique but more precise vapor pressure data, calculated a value of 51.59 C for the triple point, and it is this value which is believed to be the most accurate. The vapor pressure at the triple point is 533.0 mm Hg.

4.1.2 Vapor Pressure

A number of investigators have determined the vapor pressure of plutonium hexafluoride. Florin⁽¹⁰⁾ used a Booth-Cromer⁽³⁷⁾ null-diaphragm pressure transmitter and obtained data over the temperature range from 0 to 63 C. Mandleberg⁽¹²⁾ used a bellows manometer of the null type and obtained data over the temperature range from -29.5 to +21 C. The most careful determination of the vapor pressure of plutonium hexafluoride was made by Weinstock,⁽³⁶⁾ who used a quartz "sickle" gauge and obtained very precise data over the temperature range from 0 to 77 C. Weinstock fitted the following equations to his data:

Solid PuF_6 (0-51.59 C):

$$\log P_{\text{mm}} = - \frac{2095.0}{T} + 3.4990 \log T + 0.39024 \quad ;$$

Liquid PuF_6 (51.59-77.17 C):

$$\log P_{\text{mm}} = - \frac{1807.5}{T} - 1.5340 \log T + 12.14545 \quad .$$

A tabulation of the vapor pressure of plutonium hexafluoride at various temperatures as determined from the above equations is included in Section 7.0.

The relationship between the vapor pressures of the hexafluorides of uranium, neptunium, and plutonium has resulted in several papers which attempt to account for the observations in terms of molecular distortions in the condensed phase.⁽⁵⁷⁾

4.2 Thermodynamic Properties

At this time, no reliable experimental values for the thermodynamic constants of formation for plutonium hexafluoride are available. A summary of the thermodynamic data which have been published is shown in Table 2.

Table 2

THERMODYNAMIC CONSTANTS FOR PLUTONIUM HEXAFLUORIDE

Process	T (°K)	ΔF (kcal/mole)	ΔH (kcal/mole)	ΔS (eu)
$\text{PuF}_6(\text{s}) \rightarrow \text{PuF}_6(\text{g})$	323.9 0	- -	11.6 ^a 12.68 ^b	- -
$\text{PuF}_6(\ell) \rightarrow \text{PuF}_6(\text{g})$	335.5	-	7.0 ^a	22.0 ^c
$\text{PuF}_6(\text{s}) \rightarrow \text{PuF}_6(\ell)$	323.9	-	4.456 ^a	13.72 ^a
$\text{PuF}_4(\text{s}) + \text{F}_2(\text{g}) \rightarrow \text{PuF}_6(\text{g})$	298 548.2	6.46 ^d 6.78 ^d	- 7.09 ^d	- -1.3 ^d
$\text{Pu}(\text{s}) + 3 \text{F}_2(\text{g}) \rightarrow \text{PuF}_6(\text{g})$	298	-390.6 ^e	-411.2 ^e	-69.1 ^e

^aReference 36.^dReference 45.^bReference 55.^eSee text.^cReference 10.

Various thermodynamic functions have been calculated by Sundaram⁽³⁸⁾ from the infrared spectrum data and these are summarized in Table 3. Other calculations based on infrared data have also been reported by Nagarajan⁽³⁹⁾ and Hawkins.⁽⁴⁰⁾

Table 3

THERMODYNAMIC FUNCTIONS FOR PLUTONIUM HEXAFLUORIDE⁽³⁸⁾ FOR IDEAL GASEOUS STATE, ONE ATMOSPHERE PRESSURE

T (°K)	C_p (cal/deg-mole)	$-(H_T^\circ - H_0^\circ)/T$ (cal/deg-mole)	$-(F_T^\circ - H_0^\circ)/T$ (cal/deg-mole)	S° (cal/deg-mole)
100	17.86	11.27	50.25	61.52
200	26.45	16.95	59.93	76.88
273.16	30.10	20.05	65.69	85.74
298.16	30.99	20.92	67.47	88.39
300	31.04	20.98	67.61	88.59
400	33.45	23.79	73.98	97.77
500	34.85	25.97	79.82	105.79
600	35.66	27.49	84.56	112.05
700	36.17	28.67	88.79	117.46
800	36.53	29.66	92.82	122.58
900	36.78	30.42	96.30	126.72
1000	36.96	31.08	99.57	130.65
1100	37.08	31.60	102.49	134.09
1200	37.19	32.07	105.36	137.43
1300	37.27	32.48	107.95	140.43
1400	37.33	32.82	110.35	143.17
1500	37.39	33.13	112.77	145.90

Brewer(7) has estimated thermodynamic values for plutonium hexafluoride from the available data for the corresponding uranium compounds and the thermodynamic values for aqueous ions. He derived a value for the free energy of formation of plutonium hexafluoride of -433 kcal/mole and the heat of formation at -453 kcal/mole at 298 K. Another estimate,(31) based on the free energy of formation of plutonium tetrafluoride derived by Dawson(41) from the equilibrium of PuF_3 , O_2 , PuF_4 , and PuO_2 and Westrum's data(42) for PuF_3 , results in a free energy of formation of plutonium hexafluoride of -393 kcal/mole. The equilibrium data reported by Johns(43) for the reaction of plutonium dioxide and hydrogen fluoride to form plutonium tetrafluoride and water together with the data reported by Holley(44) for the free energy of formation of plutonium dioxide can also be used to estimate the free energy of formation of plutonium hexafluoride. If the free energy for the reaction of plutonium tetrafluoride and elemental fluorine at 298 K is taken as 6.5 kcal/mole(45) and the free energy of formation of plutonium tetrafluoride at 298 K is taken to be -397.1 kcal/mole,* the free energy of formation of gaseous plutonium hexafluoride at 298 K is -390.6 kcal/mole. By means of the data available for plutonium(46) and the spectroscopic entropy given in Table 2, an entropy change of formation for plutonium hexafluoride of -69.1 cal/(mole)(deg) can be calculated. Finally, a heat of formation of -411.2 kcal/mole can be derived from these data. Since the calculations using the data of Johns(43) do not involve the thermodynamic data for plutonium trifluoride,** it is believed that the values given in Table 2 are the best current estimates of the thermodynamic data for plutonium hexafluoride.

4.3 Mechanical Properties

4.3.1 Density

No experimental determination of the density of plutonium hexafluoride has been carried out. On the basis of the similarity between the structures of uranium hexafluoride, neptunium hexafluoride, and plutonium hexafluoride, a crystal density of approximately 5 g/cm³ is indicated for plutonium hexafluoride. The vapor density of plutonium hexafluoride was determined by Weinstock(15) and by Wagner,(47) who found the material to be monomeric in the vapor at 25 C.

*Obtained by using the data of Johns(43) and Holley(44) and using the best available data for hydrogen fluoride and water. Only a second law calculation was made.(31)

**The data for plutonium trifluoride, derived from the solution chemistry of this material, are believed to be in error because of hydration of the trifluoride.

4.4 Optical Properties

4.4.1 Ultraviolet, Visible, and Near-infrared Spectrum

Several references to the absorption spectrum of plutonium hexafluoride have appeared in the literature, but most of them are not specific. Weinstock⁽¹⁵⁾ indicated the presence of six groups of bands in the region from 5000 to 25,000 Å. Jorgensen⁽⁴⁸⁾ quotes a private communication from Weinstock that plutonium hexafluoride shows weak band groups between 3780 and 6604 cm⁻¹ (26,450-15,140 Å), six very sharp lines at 9583-10,678 cm⁻¹ (10,435-9365 Å), two band groups at 12,260 cm⁻¹ (8157 Å) and 12,720 cm⁻¹ (7862 Å), and three bands at 17,260 cm⁻¹ (5794 Å), 17,817 cm⁻¹ (5613 Å), and 18,448 cm⁻¹ (5421 Å) before the strong electron-transfer band. Goodman⁽⁴⁹⁾ has examined the absorption spectrum of gaseous plutonium hexafluoride and gives the position of many of the peaks. The absorption spectrum of gaseous plutonium hexafluoride has been examined in detail by Steindler,^(31,50) who determined the positions and extinction coefficients of the principal peaks by means of a Cary Model 14 Spectrophotometer. Table 4 lists the principal peaks in the ultraviolet, visible, and near-infrared region together with the extinction coefficients ϵ for each peak. The spectrum is shown in Figure 6, and these data are in agreement with those of Goodman.⁽⁴⁹⁾ Beer's Law plots for the absorption at 10,075 Å and at 3157 Å show no deviation from linearity, and peaks at these wavelengths may be used for quantitative analysis.

Table 4

ABSORPTION SPECTRUM OF GASEOUS PLUTONIUM HEXAFLUORIDE^(31,50)

Principal Peaks					
Instrument: Cary, Model 14, Recording Spectrophotometer					
Temperature: 22 ± 1 C					
Cell Lengths: 1 cm, 5 cm, 10 cm					
Pressures: 5-90 mm Hg					
Window: Quartz					
$\lambda(\text{Å})^a$	$\bar{\nu}(\text{cm}^{-1})$	$\epsilon^b (\ell \text{ mole}^{-1} \text{ cm}^{-1})$	$\lambda(\text{Å})^a$	$\bar{\nu}(\text{cm}^{-1})$	$\epsilon^b (\ell \text{ mole}^{-1} \text{ cm}^{-1})$
21150	4728	1.7	7500 ^c	13330	2.1
10435 ± 1	9583	11.8	5834 ^c	17140	4.1
10245 ± 1	9761	8.9	5614 ± 5	17810	7.0
10075 ± 1	9926	26.6 ^e	5418 ^c	18460	3.6
9870 ± 1	10132	3.7	4371 ± 5	22880	14.5
9734 ± 1	10273	3.2	4259 ^c	23480	13.9
9362 ± 1	10681	6.7	4139 ^c	24160	15.5
8374 ^c	11940	5.7	3157 ^d	31680	1050 ^f
8157 ± 5	12260	7.6	2500 ^d	40000	1925
7974 ^c	12540	6.3	2250 ^d	44440	2730
7860 ± 2	12720	8.5	2090 ^c	47850	3685

^aError in λ obtained as the average deviation of several scans. The wave length of all sharp peaks have been corrected by use of a standard mercury arc.

^bBased on at least 4 determinations at each peak.

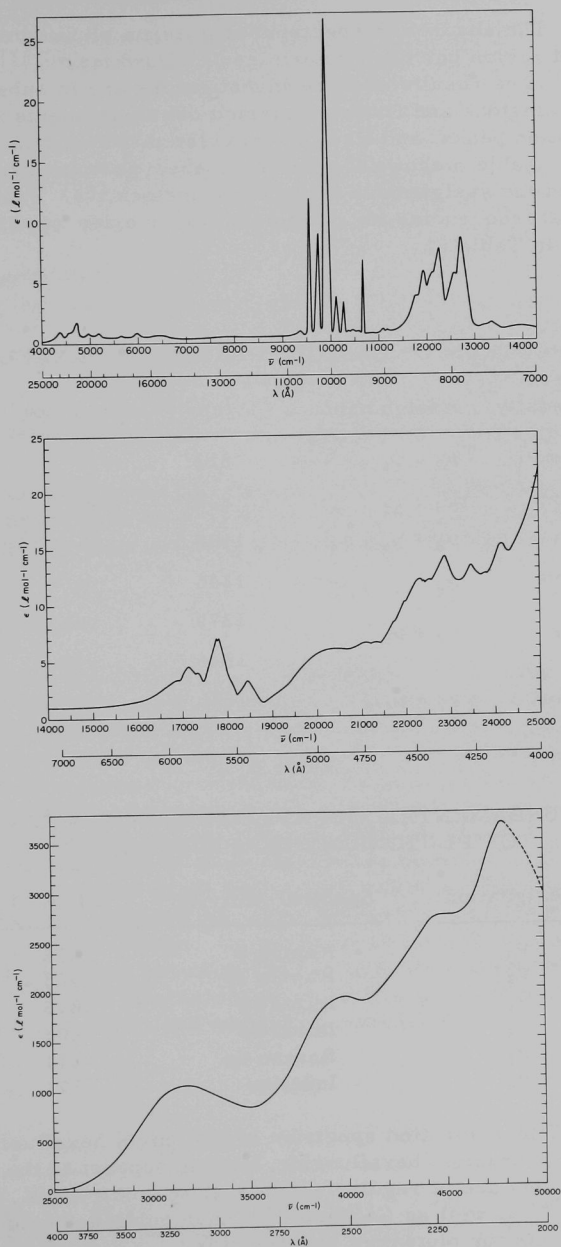
^cBroad peak.

^dVery broad peak.

^eAverage deviation ±0.6.

^fAverage deviation ±80.

Figure 6
ABSORPTION SPECTRUM OF GASEOUS PLUTONIUM HEXAFLUORIDE



4.4.2 Infrared Spectrum

The absorption spectrum of gaseous plutonium hexafluoride in the infrared region has been determined by Hawkins^(40,51) and by Weinstock.⁽⁵²⁾ The results of these investigators are in substantial agreement. Both Weinstock and Hawkins carried out assignments for the observed absorption peaks, and Hawkins calculated thermodynamic functions from his data. Table 5 shows the observed absorption peaks, their observed intensities, and the assignments given by Weinstock.⁽⁵²⁾ From these data, the fundamental frequencies for plutonium hexafluoride have been derived and are listed in Table 6.

Table 5

INFRARED SPECTRUM OF GASEOUS PLUTONIUM HEXAFLUORIDE⁽⁵²⁾

ν (cm ⁻¹)	Intensity	Assignment	ν (cm ⁻¹)	Intensity	Assignment
353	w	$\nu_2 - \nu_6$	822	w	$\nu_3 + \nu_5$
418	vw	$\nu_4 + \nu_5$	828	w	$\nu_1 + \nu_4$
530	vw	$\nu_2 + \nu_5 - \nu_4$	1138	m	$\nu_2 + \nu_3$
615	vs	ν_3	1246	m	$\nu_1 + \nu_3$
693 } 698 }	s	$\nu_2 + \nu_6$	1279	vvw	?
721 } 728 }			1346 ?	vvw	$\nu_2 + \nu_3 + \nu_5$
	m	$\nu_2 + \nu_4$	1656 ?	vvw	$2\nu_2 + \nu_3$

Table 6

FUNDAMENTAL VIBRATIONAL FREQUENCIES OF PLUTONIUM HEXAFLUORIDE⁽⁵²⁾

Designation	Spectral Activity	ν (cm ⁻¹)
ν_1	Raman p	628
ν_2	Raman dp	523
ν_3	Infrared	615
ν_4	Infrared	203
ν_5	Raman dp	211
ν_6	Inactive	171

The absorption spectrum of plutonium hexafluoride is very similar to that of uranium hexafluoride, lending support to the supposition that both molecules are of regular octahedral symmetry, i.e., point group O_h . Claasen^(53a) as well as Califano^(53b) have published calculations on the force constants for plutonium hexafluoride.

4.4.3 Raman Spectrum

It was not possible to obtain the Raman spectrum for plutonium hexafluoride because of extensive photodecomposition.^(15,52)

4.5 Magnetic Properties

The magnetic susceptibility of plutonium hexafluoride has been measured at several temperatures by Gruen.⁽⁵⁴⁾ The molar susceptibilities are shown in Table 7.

Table 7

MAGNETIC SUSCEPTIBILITY OF PLUTONIUM HEXAFLUORIDE⁽⁵⁴⁾

T (°K)	$\chi_M \times 10^6$
81	131
295	173

Gruen indicates that, based on the small susceptibility observed compared with the susceptibility of isoelectronic compounds of U (IV), Np (V) and PuO_2^{++} , which show larger, strongly temperature-dependent values, the ground electronic state of plutonium

hexafluoride is nondegenerate. Further, the first excited state of plutonium hexafluoride must be at least 1000 cm^{-1} (0.12 eV) above the ground state, which is a much greater splitting than required for the isoelectronic U (IV) compounds.

4.6 Structure

No direct determination of the structure of the plutonium hexafluoride molecule has been reported. However, the similarity of the infrared and Raman spectra of uranium and plutonium hexafluorides leads to the conclusion that the molecules are regular octahedra. Unpublished electron-diffraction measurements by Weinstock⁽⁵⁵⁾ have yielded a Pu-F distance of 1.972 \AA . Florin⁽¹⁰⁾ has reported the X-ray diffraction pattern of solid plutonium hexafluoride, and his data are shown in Table 8. The calculated data, also shown in Table 8, were obtained by Steindler and Schablaske⁽⁵⁶⁾ by matching a tabulation of all lattice data calculated for an orthorhombic cell by an IBM-704 program and using the lattice parameters for uranium hexafluoride given by Florin. On the basis of the data in Table 8, it can be assumed that plutonium hexafluoride has an orthorhombic structure in the solid phase. The cell dimensions of plutonium hexafluoride are very similar to those for uranium and neptunium hexafluoride.*

*For UF_6 ,^(59a) $a_0 = 9.900$; $b_0 = 8.966$; $c_0 = 5.207$; for NpF_6 ,⁽¹¹¹⁾ $a_0 = 9.91$, $b_0 = 8.97$ and $c_0 = 5.21$. All dimensions are in \AA .

Table 8

X-RAY DIFFRACTION DATA FOR
PLUTONIUM HEXAFLUORIDE⁽¹⁰⁾Copper K α Radiation

Observed		Calculated*(56)		
$\sin^2 \theta$	Intensity	$\sin^2 \theta$	$d(\text{\AA})$	hkl
0.0294	mw	0.02922	4.51000	020
0.0317	mw	0.03132	4.35632	210
0.0354	mw	0.03479	4.13325	111
0.0577	w	0.05670	3.23748	121
0.0760	w	0.07550	2.80551	301
0.0842	vw	0.08281	2.67892	311
0.0912	w	0.09192	2.54268	102
0.0944	vw	0.09322	2.52487	131
0.1005	vw	0.09923	2.44730	112
0.1062	w	0.10472	2.38221	321
0.1178	vw	0.11752	2.24872	401
0.1265	w	0.12526	2.17816	420
0.1428	w	0.14435	2.02902	141
0.2104	w	0.21009	1.68188	151
0.2398	w	0.23758	1.58159	601
0.2632	vw	0.26296	1.50333	060
0.3035	w	0.30332	1.39975	631
0.3394	vw	0.33846	1.32508	361
0.3589	vw	0.35900	1.28662	460

*Using the following data for the orthorhombic cell:(59b)

$$\begin{aligned}\lambda &= 1.54180 \text{ \AA} \\ a_0 &= 9.9500 \text{ \AA} \\ b_0 &= 9.0200 \text{ \AA} \\ c_0 &= 5.2600 \text{ \AA} \\ \alpha &= \beta = \gamma = 90^\circ\end{aligned}$$

4.7 Ionization Chamber Studies

Codding(58) has studied the behavior of plutonium hexafluoride as well as plutonium hexafluoride mixed with other gases in an ion chamber. Ion current measurements were made in a cylindrical nickel chamber with a ceramic insulator separating the center electrode from the chamber walls. Data relating the ion currents and gas pressures are presented for various voltage gradients for helium, fluorine, plutonium hexafluoride, and plutonium hexafluoride-helium mixtures. The source of ionizing radiation for the study with helium and fluorine was the plutonium deposited on the walls of the chamber by decomposition of plutonium hexafluoride. Saturation ion currents for mixtures of fluorine and plutonium hexafluoride are not linear combinations of the ion currents caused by each gas separately. For this reason, precise analysis of the behavior of gaseous mixtures requires a detailed calibration of the ion chamber. In addition, progressive decomposition of plutonium hexafluoride on the walls of the ion chamber would necessitate frequent recalibration of the instrument.

5.0 CHEMICAL PROPERTIES OF PLUTONIUM HEXAFLUORIDE

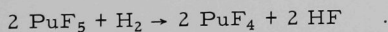
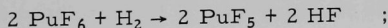
5.1 Chemical Reactions

5.1.1 Reaction with Water

Plutonium hexafluoride reacts with water to form, under controlled conditions, plutonyl fluoride (PuO_2F_2) and hydrogen fluoride. (10, 12, 15) The reaction between plutonium hexafluoride and water is very vigorous and, when carried out at room temperature using liquid water, the hydrolysis reaction is violent and may be accompanied by evolution of light. Under such severe conditions, the product of the hydrolysis includes plutonium dioxide and plutonium tetrafluoride, which are formed at the elevated temperatures of the reaction. The hydrolysis may be carried out smoothly by condensing plutonium hexafluoride onto ice at -196°C and allowing the mixture to warm slowly to room temperature. When carried out under controlled conditions, the hydrolysis of plutonium hexafluoride results in a solution in which no valence state other than Pu (VI) can be detected. (12)

5.1.2 Reaction with Hydrogen

Hawkins⁽⁶⁰⁾ indicated that plutonium hexafluoride reacts slowly with elemental hydrogen at ambient laboratory temperatures. As the final products of the reaction he obtained hydrogen fluoride and a solid which was assumed to be plutonium tetrafluoride. However, it was observed that some of the solid product which formed reacted with hydrogen. To explain this reaction, the formation of an intermediate compound, PuF_5 , was postulated. The following reactions, leading to the formation of the final product, were assumed:



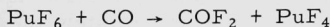
Unfortunately, neither the intermediate product nor the final product of the reaction were identified.

5.1.3 Reaction with Nitrogen

Hawkins⁽⁶¹⁾ indicated that nitrogen does not react with plutonium hexafluoride at room temperature. Wagner⁽⁴⁷⁾ at ANL observed, however, that, on prolonged standing at room temperature, nitrogen trifluoride is formed from mixtures of elemental nitrogen and plutonium hexafluoride (100 mm PuF_6 , 2250 mm N_2 , 229 days). It is not clear at this time whether the reaction is a chemical one with a very low rate or whether the reaction as observed is due to the effect of alpha particles on the mixture.

5.1.4 Reaction with Carbon Monoxide

Plutonium hexafluoride reacts with carbon monoxide⁽⁶¹⁾ at room temperature to form carbon tetrafluoride, carbon dioxide, and, presumably, plutonium tetrafluoride, although the latter was not identified. Infrared analysis of the gaseous products indicated that carbonyl fluoride (COF_2) was an intermediate in the reaction, and it is assumed that the reaction



is followed by the alpha-particle-induced decomposition of COF_2 according to the reaction

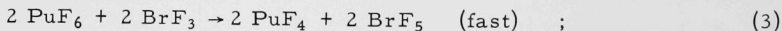
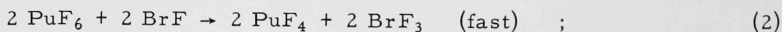
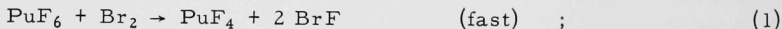


No data on the radiation stability of carbonyl fluoride are available. However, equilibrium data and thermodynamic values indicate that carbonyl fluoride may readily decompose to carbon dioxide and carbon tetrafluoride in the absence of alpha particles, particularly in nickel equipment.⁽⁶²⁾

5.1.5 Reaction with Bromine and Bromine Fluorides

5.1.5.1 Bromine

Steindler⁽⁶³⁾ found that plutonium hexafluoride reacts with gaseous bromine to form bromine pentafluoride and plutonium tetrafluoride. This gas-phase reaction proceeds relatively slowly at room temperature, but at 80 C is complete within one hour. If excess bromine is present, a slow secondary reaction between bromine and bromine pentafluoride to form bromine trifluoride is observed. It is postulated that the reaction proceeds as follows:



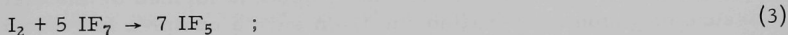
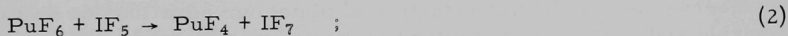
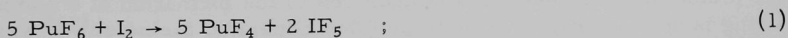
The occurrence of all but reactions (1) and (2) have been demonstrated. The occurrence of reaction (3) was demonstrated by Steindler⁽⁶³⁾ and Weinstock,⁽¹⁵⁾ and the occurrence of reaction (4) has been reported by Stein.⁽⁶⁴⁾

5.1.5.2 Bromine Trifluoride

Plutonium hexafluoride reacts with gaseous bromine trifluoride at slightly elevated temperatures to form BrF_5 and plutonium tetrafluoride.⁽⁶³⁾ Weinstock⁽¹⁵⁾ indicated that plutonium hexafluoride reacts quantitatively with bromine trifluoride and that this reaction is faster than the corresponding reaction of bromine trifluoride and elemental fluorine.

5.1.6 Reaction with Iodine

Plutonium hexafluoride reacts with elemental iodine to form iodine heptafluoride and probably plutonium tetrafluoride.⁽³¹⁾ The reaction proceeds rapidly at room temperature in the gas phase. In the presence of excess iodine, iodine pentafluoride is obtained together with a small amount of plutonium trifluoride. These results have been interpreted on the basis of the following reactions:



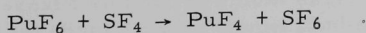
Although reaction (3) is not reported in the literature, its occurrence is not unlikely, considering the high reactivity of iodine heptafluoride and the fact that excess iodine is required to prevent the formation of iodine heptafluoride in the reaction of iodine with fluorine at room temperature.⁽⁶²⁾ The free energy for reaction (4) is estimated to be +38 kcal/mole at 298 K⁽³¹⁾ and, hence, the presence of plutonium trifluoride is not readily explained.

5.1.7 Reaction with Mercury

Plutonium hexafluoride reacts quantitatively with metallic mercury at room temperature.⁽³¹⁾ Although it is likely that one of the products is mercuric fluoride, the products of the reaction have not been identified.

5.1.8 Reaction with Sulfur Tetrafluoride

Plutonium hexafluoride reacts with sulfur tetrafluoride⁽⁶⁵⁾ according to the reaction



The reaction proceeds quantitatively at room temperature. This reaction may be used to separate uranium hexafluoride and plutonium hexafluoride since no reaction between sulfur tetrafluoride and uranium hexafluoride has been observed. Such a separation has been demonstrated.⁽⁶⁶⁾

5.1.9 Reaction with Carbon Disulfide

Plutonium hexafluoride reacts vigorously in the gas phase at room temperature with gaseous carbon disulfide.⁽⁴⁷⁾ The identified products of the reaction are plutonium tetrafluoride, sulfur tetrafluoride, sulfur hexafluoride, and carbon tetrafluoride.

5.1.10 Reaction with Calcium Fluoride

Cathers⁽⁶⁷⁾ found that plutonium hexafluoride can be trapped on calcium fluoride from a gas stream, but the experiments were carried out with very small quantities of plutonium hexafluoride. The retention of the plutonium hexafluoride was ascribed to the formation of a complex. Using larger quantities of plutonium hexafluoride, Steindler⁽³¹⁾ was unable to observe any significant retention of plutonium hexafluoride on calcium fluoride and concluded that either no complex is formed or the dissociation pressure of plutonium hexafluoride from such a complex is greater than 10^{-3} mm Hg at room temperature.

5.1.11 Reaction with Lower Plutonium Fluorides

Weinstock⁽¹⁵⁾ investigated the reaction of plutonium hexafluoride and plutonium tetrafluoride and found no fluorides other than the reagents used. The reaction of plutonium trifluoride and plutonium hexafluoride, studied by Weinstock, yielded only the tetrafluoride and no evidence for an oxidation state other than (IV) was obtained. Mandleberg⁽¹²⁾ observed a brick-red residue in the equipment used to prepare plutonium hexafluoride by fluorination of plutonium tetrafluoride. On the basis of analysis of the solid for fluorine content and an X-ray diffraction pattern said to be similar to that of U_4F_{17} , these authors conclude that the brick-red solid is Pu_4F_{17} . Hawkins⁽⁶⁸⁾ obtained a white or buff-colored solid on treatment of plutonium tetrafluoride with elemental oxygen at 800 to 950 C and, on the basis of an X-ray diffraction pattern, identified the solid as Pu_4F_{17} . Trevorrow⁽⁶⁹⁾ observed a brick-red solid product from the thermal decomposition of plutonium hexafluoride, but chemical analysis of this material⁽⁴⁵⁾ indicated clearly that the solid was plutonium tetrafluoride and not Pu_4F_{17} . Weinstock⁽¹⁵⁾ noted that the solid product of the decomposition of plutonium hexafluoride by radiation was green and turned white on exposure to air. Both of these solids were identified as plutonium tetrafluoride.

Gendre⁽¹³⁾ concluded on the basis of differences in fluorination rates of solids formed from plutonium tetrafluoride and fluorine, from reversible color changes and from a break at 370 C in the Arrhenius plot for the fluorination rates, that intermediate fluorides, particularly Pu_4F_{17} , exist. Although Brewer⁽⁷⁾ predicted the existence of a plutonium (V) fluoride, all attempts to prepare such a compound have failed. It is the opinion of the author that the data thus far presented do not establish unequivocally the existence of intermediate plutonium fluoride compounds.

5.1.12 Reaction with Uranium Tetrafluoride

Weinstock⁽¹⁵⁾ reacted plutonium hexafluoride and uranium tetrafluoride at 200 to 225 C. The products of the reaction were plutonium tetrafluoride and uranium hexafluoride, the latter reacting with uranium tetrafluoride to form U_2F_9 .

5.1.13 Reaction with Sulfuric Acid

Mandleberg^(12,70) carried out the reaction of plutonium hexafluoride and concentrated sulfuric acid. The reaction yielded plutonium (IV) sulfate; no other products were identified.

5.1.14 Reaction with Carbon Tetrachloride and Trichlorofluoromethane

Hawkins⁽⁷¹⁾ observed a rapid reaction of gaseous plutonium hexafluoride and gaseous carbon tetrachloride at 25 C. The gaseous products were identified as trichlorofluoromethane (CFCl_3) and dichlorodifluoromethane (CF_2Cl_2). The solid product was not identified but was presumed to be plutonium tetrafluoride. The reaction of plutonium hexafluoride and trichlorofluoromethane (CFCl_3) was also studied by Hawkins.⁽⁷¹⁾ The gaseous products of the reaction were difluorodichloromethane (CF_2Cl_2) and trifluoromonochloromethane (CF_3Cl). Again, the solid product of the reaction was not identified but was presumed to be plutonium tetrafluoride.

Other fluorinated compounds, such as perfluoroethane (C_2F_6), trifluoromonochloromethane (CF_3Cl), and difluorodichloromethane (CF_2Cl_2), do not react with plutonium hexafluoride at ambient laboratory temperatures.⁽⁷¹⁾

5.1.15 Miscellaneous

Brown and Hill⁽¹⁰⁵⁾ indicated that plutonium hexafluoride can be separated from uranium hexafluoride by selectively reducing plutonium hexafluoride with unspecified substances.

5.2 Reactions of Plutonium Hexafluoride with Materials of Construction

5.2.1 Nickel

The consumption of plutonium hexafluoride on nickel surfaces was studied by Grande.⁽⁷²⁾ The following list of comments represents a summary of the conclusions reached in this study:

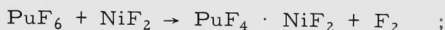
a) Prefluorination decreased the consumption of plutonium hexafluoride on nickel. The effect of prefluorination appears to follow a parabolic rate law, i.e., the consumption decreases as \sqrt{t} , where t is the time of prefluorination.

b) A double prefluorination cycle appeared to be slightly more effective than a single prefluorination in stabilizing nickel surfaces toward consumption of plutonium hexafluoride.

c) At a constant time and fluorine pressure, the effect of prefluorination temperature on the deposition of plutonium hexafluoride does not show a minimum in deposition at prefluorination temperatures up to 175 C. Prefluorination was carried out for one hour at 25 mm fluorine pressure.

d) The consumption of plutonium hexafluoride appears to be related to the square root of the fluorine pressure used in prefluorination, i.e., the consumption varies as $P_{F_2}^{-1/2}$.

e) The consumption rate of plutonium hexafluoride by nickel appears to decrease with time of exposure to plutonium hexafluoride. The consumption increases as the square root of the exposure time, indicating a parabolic rate law. The mechanism believed to be operative is



with fluorine diffusing through the consumption deposit to reach unreacted nickel. In support of this mechanism, the results of Jarry⁽⁷³⁾ also show that in the nickel-fluorine reaction fluorine diffuses through the nickel fluoride to attack the unreacted metal. Further, no dependence of consumption rate on the pressure of plutonium hexafluoride was observed. The plutonium hexafluoride consumption can be correlated with time according to the equation

$$D = at^{1/2} + b \quad ,$$

where, at 75 C and adequate prefluorination, $a = 0.71$, $b = 1.4$, t is the time in hours, and D is in units of $\mu\text{gm PuF}_6/\text{cm}^2$.

f) Consumption of plutonium hexafluoride increases with temperature and, after correction for double salt formation mentioned in the mechanism above, follows the Arrhenius plot with an activation energy of 7.65 kcal/mole.

g) No effect of added fluorine on the consumption of plutonium hexafluoride could be detected. Variation of the plutonium hexafluoride pressure at a constant fluorine pressure showed, however, a reduction in consumption with a decrease in the percent plutonium hexafluoride.

Although these studies appear to be rather complete, the limitations of temperature of prefluorination applied to the coupons by Grande are likely to be severe. Weinstock⁽⁷⁴⁾ used a rather severe pretreatment procedure consisting of reduction of the metal surface by hydrogen followed by fluorination with elemental fluorine at elevated temperatures. The results discussed by Jarry^(73,75) indicate that the rate of nickel fluoride formation at temperatures as low as 150 C should be very small, leading to incomplete surface protection. Adams⁽²⁴⁾ showed that prefluorination for 90 min at 560 C was required to prevent decomposition of plutonium hexafluoride.

Although most preparations of plutonium hexafluoride have been carried out at elevated temperatures, little information on the behavior of materials of construction at these temperatures (300 to 700 C) is available. Steindler⁽³¹⁾ examined a nickel crucible exposed to plutonium fluorides and fluorine at 700 C for 2 hr and found appreciable corrosion (1.25 mils/hr), including intergranular attack. Corrosion of materials of construction, including nickel, by elemental fluorine at elevated temperatures has been reported by Steindler.⁽⁷⁶⁾

Florin⁽⁸⁾ carried out experiments on the deposition of plutonium hexafluoride at room temperature on metal strips which had been prefluorinated at 100 C. Nickel showed the lowest increases in plutonium deposition of all materials studied, including copper, platinum, brass, silver solder and fluoroethene.

5.2.2 Copper

The consumption of plutonium hexafluoride on copper was studied by Grande.⁽⁷²⁾ The results of this study were, in general, similar to those noted for nickel with the following exceptions:

a) Copper did not show a parabolic rate law behavior in the relation between consumption and prefluorination time.

b) Copper did show an optimum prefluorination temperature of approximately 150 C, but showed a pronounced breakdown of the protective film at temperatures greater than 150 C.

c) At low pressures of fluorine in the prefluorination step, copper showed a marked departure from the inverse relation mentioned for nickel, i.e., $D \propto P_{F_2}^{-1/2}$.

d) The rate law for consumption on copper with time is

$$D = 0.68 t^{1/2} + 1.2 \quad .$$

In general, copper showed larger values for the consumption of plutonium hexafluoride than nickel, aluminum, or Monel.

5.2.3 Aluminum

The consumption of plutonium hexafluoride on aluminum was studied by Grande.⁽⁷²⁾ The results of this study were, in general, similar to those mentioned for nickel with the following exceptions:

a) Aluminum showed an optimum prefluorination temperature of approximately 150 C.

b) The rate law for the variation of consumption with prefluorination time is given by

$$D = 0.17 t^{1/2} + 0.63 \quad .$$

c) The activation energy for the consumption of plutonium hexafluoride as a function of temperature was 15.4 kcal/mole.

Aluminum generally showed a lower consumption of plutonium hexafluoride than did nickel, Monel, and, particularly, stainless steel and copper.

Hawkins⁽⁷⁷⁾ also carried out exploratory stress-corrosion experiments with aluminum alloys (7075T6, 2014T6) and concluded that there appeared no evidence for rapid corrosion of the samples by plutonium hexafluorides or fluorine at 75 C. Further, aqueous removal of consumption deposits resulted in increased corrosion of the aluminum alloy when compared with the corrosion of nonstressed samples. Owing to the lack of additional data, no definitive conclusion can be reached.

5.2.4 Stainless Steel

The consumption of plutonium hexafluoride on type 347 stainless steel was studied by Grande.⁽⁷²⁾ The results of this study were, in general, similar to those noted for nickel with the following exceptions:

a) Stainless steel did not exhibit a parabolic rate law relation between consumption and prefluorination time. On prolonged exposure to fluorine, stainless steel showed inconsistent results, primarily resulting in excessive consumption of plutonium hexafluoride.

b) Stainless steel showed an optimum prefluorination temperature of approximately 150 C.

c) The rate law for relating consumption of plutonium hexafluoride to time of exposure to stainless steel is given by

$$D = 1.2 t^{1/2} + 1.5$$

The consumption of plutonium hexafluoride by stainless steel was generally much greater than that of nickel or aluminum and was similar to that for copper.

5.2.5 Monel and Inconel

The consumption of plutonium hexafluoride on Monel and Inconel was studied by Grande,⁽⁷²⁾ who found results generally similar to those for nickel.

5.2.6 Other Materials of Construction

The following table lists the consumption of plutonium hexafluoride on several materials of construction.⁽⁷²⁾ All materials were prefluorinated for one hour at 90 C and 25 mm fluorine, and were exposed to 10 mm plutonium hexafluoride at 25 C for one hour.

Material	Consumption ($\mu\text{gm}/\text{cm}^2$)	Material	Consumption ($\mu\text{gm}/\text{cm}^2$)
Molybdenum	1.0 ± 0.2	Palladium	1.8 ± 0.2
Platinum	1.2 ± 0.1	Gold	1.8 ± 0.3
Nickel-plated Copper	1.4 ± 0.2	Silver	2.7 ± 0.3
Nickel-plated Stainless Steel	1.4 ± 0.2	Silver Solder	3.0 ± 0.5
Nickel-plated Nickel	1.4 ± 0.1	Teflon	3.9 ± 0.9
Nickel*	1.5 ± 0.1		

*Values for nickel, copper, aluminum, and Monel at 42 mm PuF_6 were 1.4 ± 0.1 , 4.6 ± 2.1 , 1.6 ± 0.2 and 1.7 ± 0.1 , respectively. Other data indicated consumption by stainless steel is similar to copper.

Several authors^(8,15) have indicated that fluorothene slowly absorbs plutonium hexafluoride at ambient laboratory temperature.

5.3 Solution Chemistry

Owing to the great reactivity of plutonium hexafluoride, inert solvents for plutonium hexafluoride must show exceptional chemical stability. Weinstock⁽¹⁵⁾ reported attempts to prepare a dilute solution of plutonium hexafluoride in n-perfluoroheptane (C_7F_{16}) which were successful only after the small amount of unfluorinated hydrogen remaining in the fluorocarbon had been removed by reaction with plutonium hexafluoride. No other information on the solution chemistry of plutonium hexafluoride has been reported.

5.4 Decomposition of Plutonium Hexafluoride by Radiation

The decomposition of plutonium hexafluoride by its own alpha radiation was observed by all investigators who handled appreciable quantities of the hexafluoride. This decomposition proved to be troublesome, particularly when samples were stored in the condensed phase. Although a number of measurements on the rates of decomposition have been published, most of the reported values, unfortunately, are accompanied by insufficient data to permit evaluation of the results. Further, only Weinstock⁽¹⁵⁾ appreciated the problems which arise when measuring rates of decomposition in a system in which equilibria are important. An extensive study of the decomposition of plutonium hexafluoride by radiation has recently been started.⁽⁷⁸⁾

5.4.1 Decomposition by Alpha Radiation

The data on the decomposition of plutonium hexafluoride by alpha radiation reported in the literature prior to the study by Steindler, Wagner, and Fischer⁽⁷⁸⁾ are summarized in Table 9. All reports indicate

Table 9

DECOMPOSITION OF PLUTONIUM HEXAFLUORIDE BY ALPHA RADIATION; SUMMARY OF REPORTED RESULTS

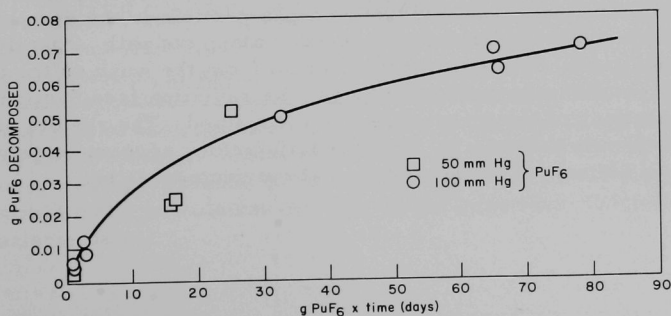
Conditions	Rate of Decomposition	Source
Solid in nickel	1.1%/day	Trevorrow ⁽⁸⁰⁾
Solid in Pyrex	1.5%/day	Weinstock ⁽¹⁵⁾
Solid-vapor ^a	0.6-1.3%/day	Florin ⁽¹⁰⁾
Solid-vapor in nickel or glass	1-2%/day	Mandleberg ⁽¹²⁾
Solid in nickel	2%/day	Steindler ⁽³¹⁾
Vapor in quartz	0.060-0.063%/day	Weinstock ⁽¹⁵⁾
Vapor in nickel	0.35%/day	Weinstock ⁽¹⁵⁾

^aMaterial of construction of containment vessel was not reported.

that the products of the decomposition are fluorine and plutonium tetrafluoride, although the colors of the solid product are reported to be pink,^(12,69) green,⁽¹⁵⁾ or the usual buff color of plutonium tetrafluoride produced by other means.⁽³¹⁾ In all cases the solid product was identified as the tetrafluoride, although Mandleberg⁽¹²⁾ indicated that a hydrate is isolated if the sample is exposed to air. This is in keeping with the observation⁽³¹⁾ that finely divided plutonium tetrafluoride, formed by the reaction of bromine trifluoride and uranium-plutonium alloys, rapidly absorbs water to form a hydrate $\text{PuF}_4 \cdot n\text{H}_2\text{O}$ ($n < 2.0$). The formation of hydrates of plutonium tetrafluoride was first reported by Dawson.⁽⁷⁹⁾

Steindler *et al.*⁽⁷⁸⁾ presented data on the decomposition of gaseous plutonium hexafluoride by alpha radiation obtained over extended periods of time. These authors used spherical vessels held at ambient laboratory temperatures and determined the loss of plutonium hexafluoride after various intervals of time. When these authors included data from experiments of long duration in their calculations, it was found that the rate of decomposition of plutonium hexafluoride decreased with time. The results are shown in Figure 7. The units of the abscissa of Figure 7 are proportional to the energy absorbed by the gas. The initial rate of decomposition at room temperature in spherical nickel vessels was approximately 0.4 percent per day. When the decomposition was carried out in quartz vessels or when carried out at 80 C in metal vessels, the rates obtained were greater than those obtained in nickel at room temperature. This increased rate is believed to be the sum of the rate of the temperature-independent decomposition by alpha particles and either the rate of the temperature-independent decomposition by alpha particles and either the rate of the thermal decomposition or the rate of reaction of plutonium hexafluoride with the container. No G values were calculated from the data, since the exact energy absorbed by the system is difficult to estimate accurately. A G value of unity was obtained by Bernhardt^(81a) for the decomposition of UF_6 by α particles.

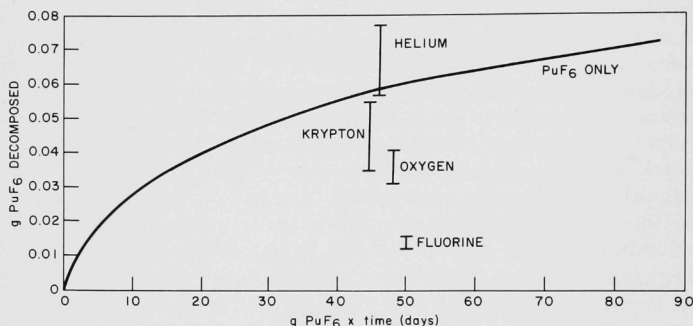
Figure 7
DECOMPOSITION OF PuF_6 BY ALPHA
RADIATION AT 25 C



The effect of added gases on the decomposition of plutonium hexafluoride by alpha particles has also been studied and preliminary results are shown in Figure 8. Fluorine reduces the decomposition, probably by enhancing the back reaction. Oxygen also appears to reduce the decomposition, but the stoichiometry is not established. The effect of krypton and helium is in agreement with results obtained on the decomposition of PuF_6 by gamma radiation (see Section 5.4.2).

Figure 8

DECOMPOSITION OF PuF_6 BY ALPHA RADIATION AT
25 C IN MIXTURES WITH INERT GASES



108-6069

In order to obtain an insight into the rates anticipated for the alpha decomposition alone, Steindler^(78,82) calculated the rates expected for gaseous plutonium hexafluoride in spherical vessels. Lind⁽⁸³⁾ has published an approximation useful in estimating the average path of an alpha particle in a spherical vessel. In order to avoid the slight inaccuracy of this approximation, a similar calculation was carried out with an IBM 704 by a Monte Carlo method. The range of alpha particles from plutonium ($E_0 = 5.15$ Mev) in plutonium hexafluoride was calculated from the Bragg-Kleeman approximation.⁽⁸⁴⁾ A numerical integration of experimental values⁽⁸⁵⁾ for the Bragg curve established the relation between percent of total path traversed by an alpha particle in the gas phase and the percent of the initial energy expended along the path. Finally, the G value used in the calculation was obtained from the work on the decomposition of plutonium hexafluoride by gamma radiation (see Section 5.4.2). The limitations of this procedure are recognized. The results of the calculation, shown in Table 10, indicate satisfactory agreement between calculated and observed values for the rate of decomposition.

Table 10

COMPARISON OF THE CALCULATED AND OBSERVED RATE
OF DECOMPOSITION OF PLUTONIUM HEXAFLUORIDE BY
ALPHA PARTICLES IN A SPHERICAL VESSEL

Energy of the Alpha Particles: 5.15 Mev
Radius of Spherical Container: 3.175 cm
G = 7 molecules/100 ev

Pressure PuF ₆ (mm Hg)	Range ^a (cm)	Decomposition (% per day)	
		Calculated	Observed
28	24.21	0.23	0.06-0.35 ^b
50	12.52	0.43	0.4 ^c
100	6.76	0.93	0.37 ^c
1000	0.67	2.92	0-
solid	0.002	3.21	0.6-2.4 ^{b,d,e}

^aRange of 5.15-Mev alpha particles in plutonium hexafluoride at the indicated pressure.

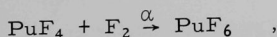
^bWeinstock, B., et al. (15)

^cWagner et al. (47)

^dSteindler, M. (31)

^eFlorin, A. (10)

The calculations have neglected the back reaction, i.e.,



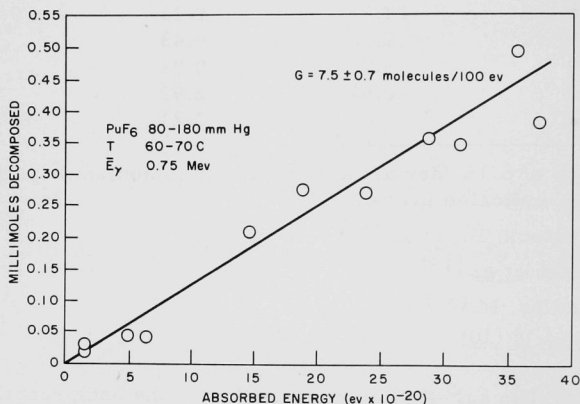
which, as was shown in Section 3.1.2.3, proceeds as written. Further, the effect of alpha particles striking the walls of the vessel has been ignored and, in the absence of data on this point, no contribution to the decomposition has been assigned to the energy expended in the walls of the container. On the other hand, alpha particles from the solid decomposition product, plutonium tetrafluoride, have been assumed to be as effective in causing decomposition as alpha particles from plutonium hexafluoride itself. Finally, spherical vessel geometry has been used for the calculation, and the rate of decomposition in vessels of other geometry would be expected to differ from the tabulated results. It may be concluded that the initial rate of decomposition of plutonium hexafluoride by alpha particles may be estimated by calculation for any vessel geometry, using the currently available data.

5.4.2 Decomposition by Gamma Radiation

The effect of gamma radiation on plutonium hexafluoride has been studied by Steindler,^(78,86) and the results are shown in Figure 9. The G value of 7.5 ± 0.7 molecules/100 ev is relatively high when compared with the G of 1 molecule/100 ev obtained by Bernhard⁽⁸¹⁾ for the alpha decomposition of uranium hexafluoride. It may be that at the temperatures of the gamma-ray experiments (60 to 70 C), thermal decomposition (Section 5.6) contributes toward the total decomposition.

Figure 9

DECOMPOSITION OF PuF_6 BY GAMMA RADIATION



108-6067

The effect of helium on the decomposition of plutonium hexafluoride by gamma radiation was found to be slight.^(78,86) Figure 10 shows the relation between the G calculated on the basis of energy absorbed in PuF_6 only for decomposition and the energy absorbed in the mixture. The G of 6.6 ± 1 is not significantly different from the value 7.5 ± 0.7 molecules/100 ev obtained in the absence of helium.

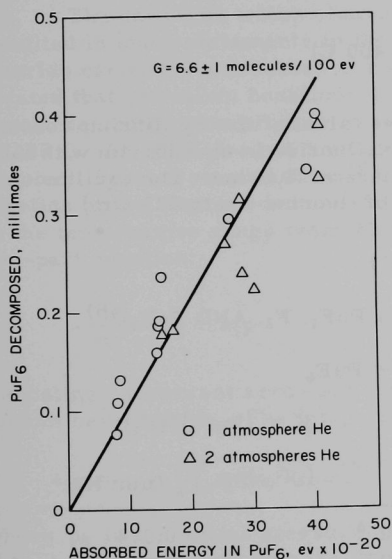
The effect of krypton, in contrast with that of helium, shows a relatively complicated behavior.⁽⁷⁸⁾ The relation between G for the decomposition and the electron fraction of krypton in plutonium hexafluoride-krypton mixtures is shown in Figure 11. While the mechanism for the decomposition of plutonium hexafluoride in mixtures with krypton has not been completely resolved, it has been suggested* that three processes

*We⁽⁷⁸⁾ are indebted to Dr. L. Dorfman for suggesting this type of mechanism to us.

may be involved. At low electron fraction of krypton, the $G\text{-PuF}_6^*$ falls due to deactivation of excited plutonium hexafluoride molecules. As the electron fraction of krypton increases, the energy absorbed by krypton also increases and energy transfer to plutonium hexafluoride becomes an important process and leads to enhanced decomposition. Finally, at large pressures and, hence, high electron fractions of krypton the mechanism becomes obscure but deactivation of a short-lived, highly excited plutonium hexafluoride molecule or an excited plutonium hexafluoride ion may account for the rapid decrease of $G\text{-PuF}_6$.

Figure 10

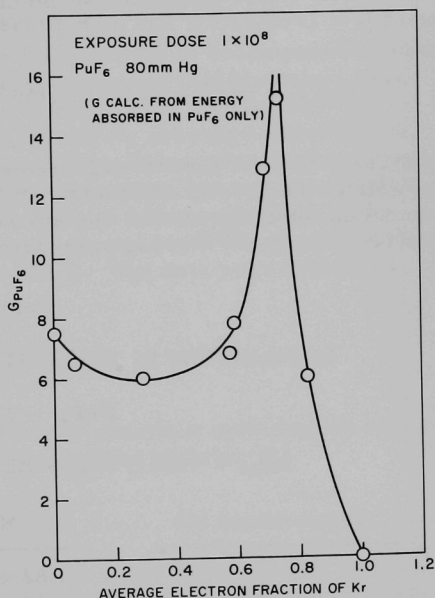
DECOMPOSITION OF PLUTONIUM HEXAFLUORIDE BY GAMMA RADIATION IN MIXTURES WITH HELIUM



108-6241

Figure 11

EFFECT OF KRYPTON ON THE DECOMPOSITION OF PuF₆



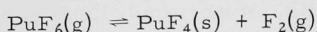
108-6072

The effects of elemental fluorine and elemental oxygen on the decomposition of plutonium hexafluoride by gamma radiation have been studied only briefly.⁽⁸⁶⁾ Oxygen appears to reduce the decomposition, but it is not known if a compound is formed, and, hence, comparison with plutonium hexafluoride alone may not be valid. Fluorine also reduces the decomposition, presumably by enhancing the back reaction.

$$* G\text{-PuF}_6 = \frac{\text{molecules PuF}_6 \text{ decomposed}}{100 \text{ ev absorbed}}$$

5.5 Equilibrium in the System PuF_6 , PuF_4 , F_2

Florin⁽¹⁰⁾ studied the equilibrium in the system



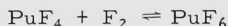
and obtained the equilibrium constant over the temperature range from 167 to 600 C. The data showed a significant break at 308 C when graphed as a van't Hoff plot. This break was stated to be suggestive of a phase change at 308 C. Weinstock⁽¹⁵⁾ reported a measurement of the equilibrium constant at 220 C. Trevor⁽⁴⁵⁾ re-examined the equilibrium in this system and carried out a careful determination of the equilibrium constant in the temperature range from 150 to 400 C. The equilibrium constant $K = (\text{PuF}_6)/(\text{F}_2)$ can be expressed by the relation

$$\log K = \frac{1331}{T(^{\circ}\text{K})} - 0.275 \quad (150 \text{ to } 400 \text{ C}) \quad ,$$

and Table 11 lists several representative values of the equilibrium constant as well as the pressure of plutonium hexafluoride in equilibrium with solid plutonium tetrafluoride and one atmosphere of fluorine. The equilibrium has been checked⁽⁸⁷⁾ at high pressures of fluorine (up to 825 atm) and was

Table 11

EQUILIBRIUM IN THE SYSTEM PuF_4 , F_2 , AND PuF_6 ⁽⁴⁵⁾



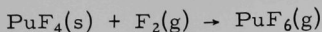
$$\log_{10} = -1331/T(^{\circ}\text{K}) - 0.275 \quad K = (\text{PuF}_6)/(\text{F}_2)$$

Temperature (C)	K	P_{PuF_6} (mm Hg)*
25	1.82×10^{-5}	0.014
100	1.44×10^{-4}	0.11
300	2.52×10^{-3}	1.9
500**	1.01×10^{-2}	7.7
600**	1.58×10^{-2}	12.0

*With 760 mm Hg F_2 .

**Extrapolated beyond the stated range for the equation, but agreement with data of Florin⁽¹⁰⁾ is satisfactory (10%).

shown to be pressure independent. The free energy for the reaction



can be calculated from the equation

$$\Delta F^\circ = -RT \ln K = 6.09 \times 10^3 + 1.26T(^{\circ}\text{K}) \text{ cal/mole}$$

The calculated value of ΔF° at 275 C is 6.78 ± 0.09 kcal/mole. The mean ΔH° for the reaction is 6.09 ± 0.14 kcal/mole, and the mean value for ΔS° for the reaction is -1.3 ± 0.2 e. u. The uncertainties listed are probable errors.

5.6 Thermal Decomposition of Plutonium Hexafluoride

The ease with which plutonium hexafluoride is decomposed by heat resulted in many statements in the early literature that plutonium hexafluoride cannot be maintained at room temperature. Weinstock⁽¹⁵⁾ indicated that plutonium hexafluoride at 50 mm Hg pressure showed little, if any, decomposition product on the walls of a Pyrex vessel after 30 min at 208 C. At 280 C for one hour, the decomposition was nearly complete. Fischer, Trevorrow, and Shinn⁽⁸⁸⁾ carried out a thorough study of the kinetics of the thermal decomposition of gaseous plutonium hexafluoride in the temperature range from 140 to 173 C. The data were fitted to a two-part equation:

$$-\frac{dp}{dt} = k_0 + k_1 p$$

indicating concurrent zero- and first-order reactions with respect to plutonium hexafluoride. The integrated form of the equation is

$$p = p_0 e^{-k_1 t} + (k_0/k_1) e^{-k_1 t} - (k_0/k_1)$$

where p_0 is the initial pressure (cm Hg), p is the pressure (cm Hg) at time t , and k_0 and k_1 are the zero-order and first-order rate constants. These constants are given by the equations

$$\log k_0 = 7.124 - \frac{3469}{T(^{\circ}\text{K})}; \quad \log k_1 = 7.260 - \frac{4292}{T(^{\circ}\text{K})}$$

and yield activation energies of 15.9 ± 1.5 kcal/mole and 19.6 ± 0.7 kcal/mole, respectively. The variation of the zero-order rate constant with the quantity of plutonium tetrafluoride is shown in Figure 12.⁽³³⁾ The mechanism proposed on the basis of these results is a homogeneous, uni-molecular decomposition of plutonium hexafluoride in the gas phase together with a heterogeneous decomposition on the surface of the plutonium tetrafluoride.

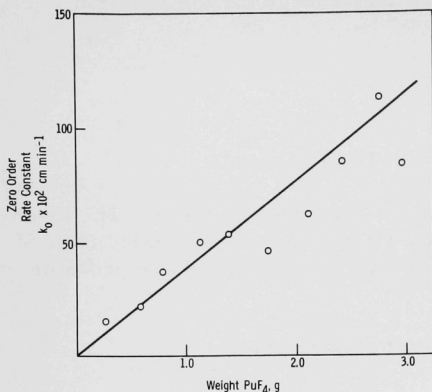


Figure 12

VARIATION OF ZERO-ORDER RATE CONSTANT
WITH WEIGHT OF PLUTONIUM TETRAFLUORIDE
IN PACKED REACTION VESSEL

108-3878

Trevorrow⁽¹⁰⁹⁾ also determined the rate of decomposition of plutonium hexafluoride at 80 C, but obtained rates lower than would be predicted from the above data. The discrepancy was attributed to differences in the heterogeneous decomposition, since the surface area of plutonium tetrafluoride in the system was not known.

Fischer⁽³³⁾ and coworkers investigated the thermal decomposition of plutonium hexafluoride in order to obtain data useful in the separation of plutonium hexafluoride from uranium hexafluoride. Static experiments, carried out at 161 C, showed good agreement with the data from the kinetic study. Experiments carried out in a flow system at temperatures between 144 and 244 C in the presence of approximately 600 mm Hg fluorine indicated only a slight effect of fluorine on the rate of decomposition of plutonium hexafluoride.

Trevorrow⁽⁸⁹⁾ has utilized the thermal decomposition of plutonium hexafluoride to effect a separation of plutonium hexafluoride from uranium hexafluoride. When a gaseous mixture of the hexafluorides is passed through a heated, pretreated vessel packed with nickel wool, plutonium hexafluoride is converted to the nonvolatile plutonium tetrafluoride. On the basis of the results of the experiments and noting that at elevated temperatures uranium also appeared in the solid residue, it was concluded that temperatures between 200 and 300 C can be used to obtain practical rates of separation.

6.0 EVALUATION AND CONTROL OF HAZARDS FROM PLUTONIUM HEXAFLUORIDE

6.1 Radiation Hazards from Plutonium Hexafluoride

The problems associated with the handling of plutonium have received considerable attention, and a summary of current information has been assembled by Steindler.⁽⁹⁰⁾ Two aspects of the radiological physics of plutonium warrant further discussion. One is the high toxicity of plutonium or internal hazard, which requires the use of gloved enclosures ("glove boxes") of unusual integrity. Although some of the work with plutonium hexafluoride has been carried out outside such enclosures, most of the current work with appreciable quantities of material is done within such boxes. The second is an external hazard from the radiation originating with the several isotopes of plutonium normally present in samples of this material.

The high toxicity of plutonium may be illustrated by data shown in Table 12, taken from Ref. 91. The very low concentrations and quantities indicated in the table require stringent regulations regarding contamination levels tolerated in laboratories. While specific techniques and policies vary from laboratory to laboratory, certain generalizations on the handling of plutonium can be made.⁽⁹²⁾ Techniques applicable to the detection of plutonium are relatively well known and documented,⁽⁹³⁾ and need no elaboration here. The high toxicity of plutonium and, hence, of plutonium hexafluoride, coupled with the volatility of the compound and its high chemical reactivity make it necessary to use both well-developed monitoring techniques and highly efficient precautions in order to assure safety in experimentation with plutonium hexafluoride.

Table 12

MAXIMUM PERMISSIBLE BODY BURDENS AND MAXIMUM PERMISSIBLE CONCENTRATIONS OF PLUTONIUM IN AIR AND WATER⁽⁹¹⁾

Isotope	Form	Critical Organ	MPBB ^a		MPC ^b per 40-hr week	
			(μc)	(μg)	Water ($\mu\text{c/cc}$)	Air ($\mu\text{c/cc}$)
Pu ²³⁸	Sol	Bone	0.04	2.4×10^{-3}	10^{-4}	2×10^{-12}
Pu ²³⁹	Sol	Bone	0.04	0.65	10^{-4}	2×10^{-12}
	Insol	Lungs ^c	0.008	0.13	-	2×10^{-12}
Pu ²⁴⁰	Sol	Bone	0.04	0.18	10^{-4}	2×10^{-12}
Pu ²⁴¹	Sol	Bone	0.9	8.2×10^{-3}	7×10^{-3}	9×10^{-11}
Pu ²⁴²	Sol	Bone	0.05	12.8	10^{-4}	2×10^{-12}

^aMaximum permissible total body burden in μc or μg .

^bMaximum permissible concentration in $\mu\text{c/cm}^3$.

^cThe low value for insoluble plutonium-239 is quoted in an earlier edition of Ref. 91 (Handbook 52, 1953) and is still used, even though it is not included in Ref. 91.

The external hazards associated with plutonium hexafluoride stem from the radiations from the several isotopes of plutonium. Samples of plutonium produced in nuclear reactors will usually consist of mixtures of several isotopes. Figure 13 illustrates the mode of formation of the isotopes of plutonium by neutron irradiation of uranium. Although Pu²³⁹ is usually the most abundant isotope of plutonium found, radiations from the other isotopes, particularly from Pu²⁴⁰, Pu²⁴¹ and Pu²³⁸, are important in assessing the external hazard. Table 13, taken from the compendium by Strominger,(94) shows the nuclear constants for the isotopes of plutonium.

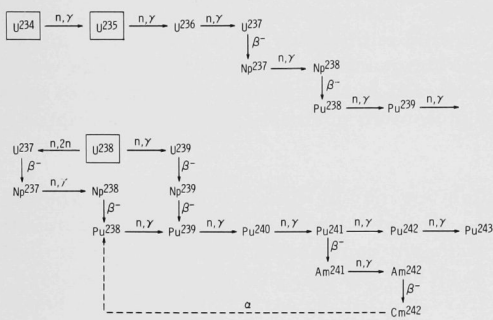


Figure 13
FORMATION OF PLUTONIUM
ISOTOPES FROM URANIUM
IN NUCLEAR REACTORS

Table 13
DECAY CONSTANTS FOR SELECTED ISOTOPES OF PLUTONIUM(94)

Isotope	Half-life (yr)	Specific Activity (d/sec-g)	E _{α,β} (Mev)	E _γ (Mev) ^a
Alpha Decay				
Pu ²³⁸	86.4	6.43 × 10 ¹¹	5.495, 72%	0.013 (0.038%)
			5.452, 28%	0.099 (0.009%)
				0.150 (0.001%)
Pu ²³⁹	2.436 × 10 ⁴	2.27 × 10 ⁹	5.147, 72.5%	0.038 (0.002%)
			5.134, 16.8%	0.052 (0.007%)
			5.096, 10.7%	0.120 (0.002%)
Pu ²⁴⁰	6.58 × 10 ³	8.38 × 10 ⁹	5.162, 76%	0.045 -
			5.118, 24%	
Pu ²⁴¹	13.3	4.12 × 10 ¹²	0.0208 β	0.145 (7%)
	5.72 × 10 ⁵ (36)		4.9 α	
Pu ²⁴²	3.79 × 10 ⁵	1.44 × 10 ⁸	4.898, 76%	
			4.858, 24%	
Spontaneous Fission			<u>ν̄(n/d)^c</u>	
Pu ²³⁸	3.8 × 10 ¹⁰	1.45 × 10 ³	2.33	
Pu ²³⁹	5.5 × 10 ¹⁵	1.0 × 10 ⁻²	(2.3) ^b	
Pu ²⁴⁰	1.22 × 10 ¹¹	4.52 × 10 ²	2.25	
Pu ²⁴²	7.1 × 10 ¹⁰	7.8 × 10 ²	2.18	

^aValues in parentheses are absolute intensities, i.e., unconverted photons per 100 disintegrations.

^bEstimated.

^cHicks, D. A., Phys. Rev., 101, 1016 (1956).

In order to illustrate the importance of the radiation from plutonium to the external hazard, Table 14 lists calculated dose rates, computed by Roesch⁽⁹⁵⁾ and by Birchall⁽⁹⁶⁾ for massive plutonium. The gamma-ray spectrum from a sample of plutonium tetrafluoride has been analyzed by Steindler.⁽⁹⁷⁾ The data permit evaluation of shielding requirements needed for larger quantities of plutonium fluorides. The major peaks observed in the gamma-ray spectrum are tabulated in Table 15 and Figure 14. It can be assumed that the gamma-ray spectrum of plutonium hexafluoride is similar to that for plutonium tetrafluoride. Berard⁽³⁴⁾ describes the detection of plutonium by gamma counting, but the precision of this method is very low. Berard also determined the gamma spectrum of plutonium

Table 14

SURFACE DOSE RATES FROM MASSIVE PLUTONIUM

Isotope	Radiation and Energy	Surface Dose Rate (rad/hr)	
		Roesch ⁽⁹⁵⁾	Birchall ⁽⁹⁶⁾
Pu ²³⁸	X ray (~20 kev)	980	736
	Gamma ~45 kev	2	6.95
	150 kev	-	1.87
	100 kev	-	13.3
		982	758
Pu ²³⁹	X ray (~20 kev)	0.61	0.751
	Gamma (several)	0.056	-
	38 kev	-	0.001
	52 kev	-	0.006
	120-207 kev	-	0.013
	380 kev	-	0.302
		0.666	1.073
Pu ²⁴⁰	X ray (~20 kev)	14	7.2
	Gamma 44 kev	0.008	0.02
	1 Mev (spont. fiss.)	0.37	-
		14.38	7.22
Pu ^{241a}	Gamma 100 kev	-	10.04
	145 kev	-	2.37
			12.37
Pu ²⁴²	X ray (~17 kev)	-	0.06
Am ^{241a}	X ray 17 kev	742.5 ^b	-
	26 kev	22.7	33
	43 kev	6.5	-
	Gamma 60 kev	713	2680
	99 kev	16	-
		1483 ^c	2713
U ^{237c}	Beta 250 kev	-	3.0 × 10 ⁸
	Gamma 60 kev	-	0.61 × 10 ⁸
	210 kev	-	5.91 × 10 ⁸
	330 kev	3.92 × 10 ^{8c}	1.77 × 10 ⁸
		3.92 × 10 ⁸	11.3 × 10 ⁸

^aThe growth of Am²⁴¹ from Pu²⁴¹ can be approximated by the equation;⁽⁹⁵⁾
 $\text{Am}^{241}(\text{curies/g of initially pure Pu}^{241}) = 4.28 \times 10^{-4}t$ for t (days) \ll 14 years.

^bRoesch assumed a source density of 1 c/g. The data have been converted where appropriate to obtain comparable figures.

^cThe growth of U²³⁷ from Pu²⁴¹ can be approximated by the equation;⁽⁹⁵⁾
 $\text{U}^{237}(\text{curies/g of initially pure Pu}^{241}) = 4.7 \times 10^{-3} [1 - \exp(-0.102t)]$ for
 t (days) \ll 14 years.

hexafluoride up to a gamma energy of 400 kev. These data are in substantial agreement with those presented by Steindler for plutonium tetrafluoride.⁽⁹⁷⁾

Table 15

OBSERVED GAMMA SPECTRUM OF PLUTONIUM TETRAFLUORIDE⁽⁹⁷⁾

4 x 4-in. NaI(Tl) crystal, 256-channel analyzer,
~45% geometry, no absorber other than
sample container.

E (kev) ^a	Relative Peak Height ^b	Comments	E (kev) ^a	Relative Peak Height ^b	Comments
17	0.21	Highly attenuated, X-ray shoulder on 30-kev peak	200	0.17	F ¹⁹ (196)
30	0.8	Pu ²³⁹ (37) ^c	380	0.07	Pu ²³⁹ (380) broad
60	4.7	Am ²⁴¹ (60), Pu ²³⁹ (52)	500	0.014	Na ²² (511) annihilation shoulder
100	1.00	U ²³⁸ X-ray, F ¹⁹ (109), Pu ²³⁹ (120)	850	0.002	-
130	0.70	Shoulder of 100 kev	1200	0.0003	Na ²² (1276)
160	0.33	Shoulder of 100 kev	1700	0.0004	Na ²² (1787)
			1950	0.0001	-

^aApproximate

^bThe 100-kev peak was arbitrarily chosen as unity.

^c(37), etc. = energy (kev) where element is expected to appear.

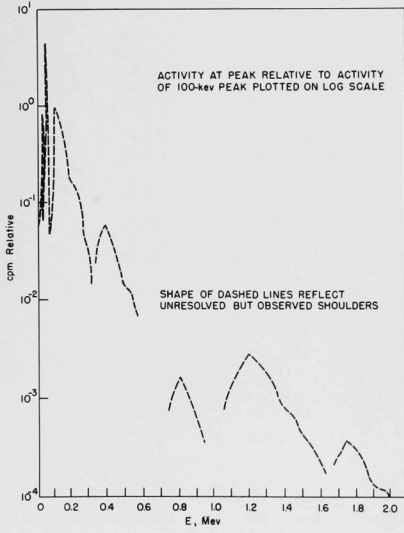


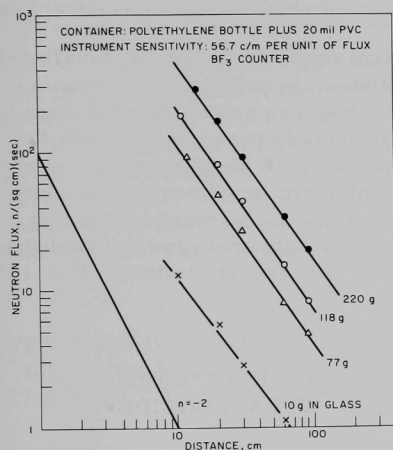
Figure 14
GAMMA SPECTRUM OF PLUTO-
NIUM TETRAFLUORIDE⁽⁹⁷⁾
4 x 4-in. NaI(Tl) Crystal, 256-Channel
Analyzer, ~45% Geometry,
No Absorber Other Than
Sample Container

One of the important sources of external hazard from plutonium fluorides is the fast-neutron flux generated by the reaction of plutonium alpha particles on fluorine, i.e., F¹⁹ (α ,n) Na²². Although no experimental

measurements of the neutron flux from plutonium hexafluoride have been published, a few measurements are available for plutonium tetrafluoride.

Figure 15

NEUTRON MEASUREMENTS ON PLUTONIUM TETRAFLUORIDE⁽⁹⁷⁾



Helgeson⁽⁹⁸⁾ has published the results of measurements reported in biological units (rem/h) but does not give values for the neutron flux. Steindler⁽⁹⁷⁾ obtained data on the neutron flux from samples of plutonium tetrafluoride at various amounts of plutonium tetrafluoride. A summary of the data is shown in Figure 15.

It is possible to calculate the expected neutron flux from plutonium fluorides, though accurate values for the yield integral for fluorine are not available. Such calculations have been made by Steindler⁽⁹⁰⁾ by means of appropriate estimates. Table 16 summarizes the results of these calculations. These data permit estimation of neutron dose rates from samples of plutonium tetrafluoride. Conversion of these data to plutonium hexafluoride requires the density and fluorine content of plutonium hexafluoride. The greater fluorine

content (per molecule) and the lower crystal density of plutonium hexafluoride compared with the tetrafluoride result in values of the calculated

Table 16

FAST-NEUTRON EMISSION FROM METALLIC PLUTONIUM AND SELECTED COMPOUNDS⁽⁹⁰⁾

Substance	n/sec-g Pu		ϕ from 500-g Sphere ^c (n/cm ² -sec)	
	(α, n) ^a	Spontaneous Fission ^b	(S.F.) ^d	(α, n)
Pu ²³⁸	-	3.4×10^3	6.1×10^4	-
Pu ²³⁸ F ₄	2.1×10^6	-	2.3×10^4	1.4×10^7
Pu ²³⁸ O ₂	1.4×10^4	-	3.3×10^4	1.3×10^5
Pu ²³⁹	-	0.02	0.4	-
Pu ²³⁹ F ₄	4.3×10^3	-	0.13	2.9×10^4
Pu ²³⁹ O ₂	45	-	0.20	4.4×10^2
Pu ²⁴⁰	-	1×10^3	1.8×10^4	-
Pu ²⁴⁰ F ₄	1.6×10^4	-	6.9×10^3	1.1×10^5
Pu ²⁴⁰ O ₂	170	-	1×10^4	1.6×10^3
Pu ²⁴²	-	1.7×10^3	3.1×10^4	-
Pu ²⁴² F ₄	1.7×10^2	-	1.1×10^4	1.2×10^3
Pu ²⁴² O ₂	2.7	-	1.7×10^4	27

^aThe following yield integral values were used: ($\times 10^6$)

Pu²³⁸, F - 14; O - 0.18; Pu²³⁹, F - 8; O - 0.17;

Pu²⁴⁰, F - 8; O - 0.17; Pu²⁴¹, F - 5; O - 0.16.

^bSee Table 12 for constants.

^cFast-neutron flux at the surface of a 500-g sphere of the indicated compound at its crystal density, passing through a sphere of unit cross-sectional area.

^dSpontaneous Fission.

neutron flux from plutonium hexafluoride which are essentially the same as that from plutonium tetrafluoride. Thus, a 500-g sphere of plutonium tetrafluoride has a calculated surface neutron flux of 2.9×10^4 n_f/cm^2 -sec, whereas a 500-g sphere of plutonium hexafluoride has a calculated surface neutron flux of 2.8×10^4 n_f/cm^2 -sec. The average energy of the neutrons from the α, n reaction is approximately 1 Mev, and a biological dose of 0.14 mrem/h is equivalent to 1 n_f/cm^2 sec.⁽⁹⁹⁾

6.2 Criticality Considerations

No experimental data on the critical mass of plutonium hexafluoride are available. The critical radii for plutonium hexafluoride have been calculated by Tralli⁽¹⁰⁰⁾ by means of a multigroup calculation for bare spheres and one-group calculations for reflected spheres. The data for infinite cylinders were obtained by use of the same buckling as for spheres. The results of the calculations for both plutonium hexafluoride and plutonium tetrafluoride are given in Table 17. It should be emphasized that the data in Table 17 are calculated values and are subject to error. Additional information on criticality may be obtained from reports listed in Ref. 101.

Table 17

CRITICAL RADII CALCULATED FOR PLUTONIUM HEXAFLUORIDE AND PLUTONIUM TETRAFLUORIDE⁽¹⁰⁰⁾

	Critical Radii (in.)	
	PuF ₆	PuF ₄
Bare sphere	8.77	6.54
Bare infinite cylinder	6.72	5.00
5-in. iron reflector-sphere	6.25	4.68
5-in. iron reflector-infinite cylinder	4.78	3.58
10-in. iron reflector-sphere	5.50	-
10-in. aluminum reflector-sphere	6.07	-

6.3 Glove Box Operations

In order to assure containment of plutonium hexafluoride, enclosures of high integrity are normally employed. Considerable development of gloved enclosures has been carried out because of the importance of plutonium in the atomic energy field. A recent report⁽¹⁰²⁾ summarizes the construction practices for gloved boxes at several laboratories. The operation of equipment within the enclosures and the construction of equipment suitable for plutonium hexafluoride have, in general, been a matter

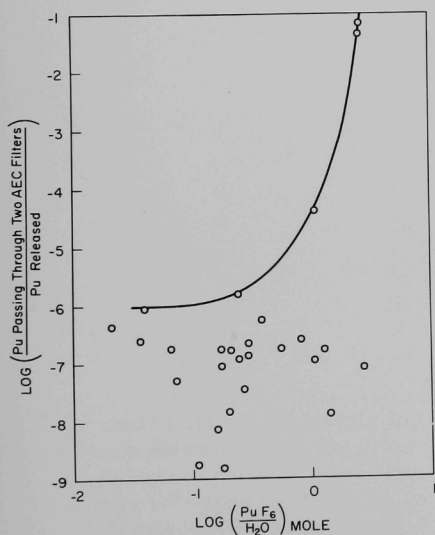
of individual choice, and little published information specifically oriented to these questions has appeared. The interested reader is referred to the references cited throughout this review for details on particular apparatus and techniques. Certain experimental procedures generally useful for work in glove boxes have been summarized by Barton^(92b) and by Steindler.^(92a) A description of a pilot-plant facility for handling plutonium hexafluoride has been issued by Vogel.⁽¹⁰³⁾

6.4 Filtration of Particles from the Hydrolysis of Plutonium Hexafluoride

When plutonium hexafluoride is released into ambient laboratory air, hydrolysis takes place very rapidly and a smoke of solid hydrolysis product (PuO_2F_2) is produced. In the event that such a release is accidental, it is important to establish the efficiency with which the released particles are filtered from the air used to ventilate the glove box. Experiments have been carried out by Kessie⁽¹⁰⁴⁾ in which gaseous plutonium hexafluoride is released into an air-filled chamber in which hydrolysis takes place. The mixture of hydrolysis products and air is then drawn

through a series of test filters, and plutonium retention on these filters is measured radiometrically. Examination of the material deposited on the filters indicated that most of the hydrolyzed plutonium hexafluoride was deposited as agglomerates. The agglomerates were found to have a variety of sizes and were composed of spherical particles from 0.01 to 0.2 μ in diameter. The average particle size was found to be 0.02 μ .

Figure 16
FRACTION OF RELEASED PLUTONIUM HEXAFLUORIDE PASSING THROUGH TWO AEC FILTERS⁽¹⁰⁵⁾



b) The efficiency of AEC filter media in series is not equal to the product of their individual efficiencies.

c) The effect of moisture content of the air influences the penetration of plutonium hexafluoride through the filter media. Optimum filtration takes place only if more than the stoichiometric quantity of water is present in the air.

7.0 APPENDIX

7.1 Vapor Pressure Table for Plutonium Hexafluoride (-10 to +100 C)

The vapor pressure of plutonium hexafluoride was calculated from the equations given by Weinstock⁽³⁶⁾ over the range from -10 to 100 C. These data are tabulated in Table 18.

7.2 Vapor Pressure Table for Plutonium Hexafluoride (50-100 C in 0.1 C)

Table 19 represents an expanded list of vapor pressures of plutonium hexafluoride from 50 C to +100 C in intervals of 0.1 C, taken from the data of Weinstock.⁽³⁶⁾

Table 18
VAPOR PRESSURES FOR PLUTONIUM HEXAFLUORIDE

T (C)	P (MM)	LOGP (MM)	1/T (K)
-10.00	7.89	0.89728	3.800E-03
-9.00	8.57	0.93319	3.786E-03
-8.00	9.31	0.96884	3.771E-03
-7.00	10.10	1.00425	3.757E-03
-6.00	10.95	1.03941	3.743E-03
-5.00	11.87	1.07433	3.729E-03
-4.00	12.85	1.10902	3.715E-03
-3.00	13.91	1.14347	3.702E-03
-2.00	15.05	1.17768	3.688E-03
-1.00	16.28	1.21166	3.674E-03
-0.	17.60	1.24542	3.661E-03
1.00	19.01	1.27895	3.648E-03
2.00	20.52	1.31226	3.634E-03
3.00	22.15	1.34534	3.621E-03
4.00	23.89	1.37821	3.608E-03
5.00	25.75	1.41086	3.595E-03
6.00	27.75	1.44329	3.582E-03
7.00	29.89	1.47551	3.570E-03
8.00	32.18	1.50753	3.557E-03
9.00	34.62	1.53933	3.544E-03
10.00	37.23	1.57093	3.532E-03
11.00	40.02	1.60233	3.519E-03
12.00	43.01	1.63352	3.507E-03
13.00	46.19	1.66452	3.495E-03
14.00	49.58	1.69531	3.483E-03
15.00	53.20	1.72592	3.470E-03
15.50	55.10	1.74115	3.464E-03
16.00	57.06	1.75633	3.458E-03

Table 18 (Contd.)

T (C)	P (MM)	LOGP (MM)	1/T (K)
16.50	59.08	1.77146	3.452E-03
17.00	61.17	1.78654	3.446E-03
17.50	63.33	1.80158	3.441E-03
18.00	65.55	1.81657	3.435E-03
18.50	67.84	1.83151	3.429E-03
19.00	70.21	1.84641	3.423E-03
19.50	72.65	1.86126	3.417E-03
20.00	75.17	1.87607	3.411E-03
20.20	76.20	1.88197	3.409E-03
20.40	77.25	1.88788	3.407E-03
20.60	78.30	1.89377	3.404E-03
20.80	79.37	1.89966	3.402E-03
21.00	80.45	1.90554	3.400E-03
21.20	81.55	1.91141	3.397E-03
21.40	82.66	1.91727	3.395E-03
21.60	83.78	1.92313	3.393E-03
21.80	84.91	1.92898	3.390E-03
22.00	86.06	1.93482	3.388E-03
22.20	87.23	1.94066	3.386E-03
22.40	88.41	1.94649	3.384E-03
22.60	89.60	1.95231	3.381E-03
22.80	90.81	1.95812	3.379E-03
23.00	92.03	1.96393	3.377E-03
23.20	93.27	1.96973	3.374E-03
23.40	94.52	1.97552	3.372E-03
23.60	95.79	1.98131	3.370E-03
23.80	97.07	1.98709	3.368E-03
24.00	98.37	1.99286	3.365E-03

Table 18 (Contd.)

T(C)	P(MM)	LOGP(MM)	1/T(K)
24.20	99.68	1.99863	3.363E-03
24.40	101.01	2.00438	3.361E-03
24.60	102.36	2.01013	3.359E-03
24.80	103.72	2.01588	3.356E-03
25.00	105.10	2.02161	3.354E-03
25.20	106.50	2.02734	3.352E-03
25.40	107.91	2.03306	3.350E-03
25.60	109.34	2.03878	3.347E-03
25.80	110.79	2.04449	3.345E-03
26.00	112.25	2.05019	3.343E-03
26.20	113.73	2.05588	3.341E-03
26.40	115.23	2.06157	3.338E-03
26.60	116.75	2.06725	3.336E-03
26.80	118.28	2.07293	3.334E-03
27.00	119.84	2.07859	3.332E-03
27.20	121.41	2.08425	3.329E-03
27.40	123.00	2.08991	3.327E-03
27.60	124.61	2.09555	3.325E-03
27.80	126.24	2.10119	3.323E-03
28.00	127.89	2.10683	3.321E-03
28.20	129.55	2.11245	3.318E-03
28.40	131.24	2.11807	3.316E-03
28.60	132.95	2.12368	3.314E-03
28.80	134.68	2.12929	3.312E-03
29.00	136.42	2.13489	3.310E-03
29.20	138.19	2.14048	3.307E-03
29.40	139.98	2.14606	3.305E-03
29.60	141.79	2.15164	3.303E-03

Table 18 (Contd.)

T(C)	P(MM)	LOGP(MM)	1/T(K)
29.80	143.62	2.15721	3.301E-03
30.00	145.47	2.16278	3.299E-03
30.50	150.20	2.17666	3.293E-03
31.00	155.06	2.19051	3.288E-03
31.50	160.07	2.20431	3.282E-03
32.00	165.22	2.21807	3.277E-03
32.50	170.52	2.23179	3.272E-03
33.00	175.98	2.24546	3.266E-03
33.50	181.59	2.25910	3.261E-03
34.00	187.37	2.27270	3.256E-03
34.50	193.31	2.28625	3.250E-03
35.00	199.42	2.29977	3.245E-03
35.50	205.71	2.31325	3.240E-03
36.00	212.17	2.32669	3.235E-03
36.50	218.82	2.34008	3.229E-03
37.00	225.65	2.35344	3.224E-03
37.50	232.68	2.36676	3.219E-03
38.00	239.91	2.38004	3.214E-03
38.50	247.34	2.39329	3.209E-03
39.00	254.97	2.40649	3.204E-03
39.50	262.82	2.41966	3.198E-03
40.00	270.88	2.43278	3.193E-03
41.00	287.69	2.45892	3.183E-03
42.00	305.43	2.48491	3.173E-03
43.00	324.16	2.51075	3.163E-03
44.00	343.91	2.53645	3.153E-03
45.00	364.75	2.56199	3.143E-03
46.00	386.72	2.58740	3.133E-03

Table 18 (Contd.)

T (C)	P (MM)	LOGP (MM)	1/T (K)
47.00	409.88	2.61265	3.124E-03
48.00	434.28	2.63777	3.114E-03
49.00	459.98	2.66274	3.104E-03
50.00	487.05	2.68758	3.095E-03
51.00	515.55	2.71227	3.085E-03
52.00	540.69	2.73295	3.076E-03
53.00	559.68	2.74794	3.066E-03
54.00	579.22	2.76284	3.057E-03
55.00	599.30	2.77765	3.047E-03
56.00	619.95	2.79235	3.038E-03
57.00	641.16	2.80697	3.029E-03
58.00	662.96	2.82148	3.020E-03
59.00	685.34	2.83591	3.011E-03
60.00	708.34	2.85024	3.002E-03
61.00	731.95	2.86448	2.993E-03
62.00	756.19	2.87863	2.984E-03
63.00	781.07	2.89269	2.975E-03
64.00	806.60	2.90666	2.966E-03
65.00	832.80	2.92054	2.957E-03
66.00	859.67	2.93433	2.949E-03
67.00	887.24	2.94804	2.940E-03
68.00	915.50	2.96166	2.931E-03
69.00	944.49	2.97520	2.923E-03
70.00	974.20	2.98865	2.914E-03
71.00	1004.65	3.00201	2.906E-03
72.00	1035.85	3.01530	2.897E-03
73.00	1067.82	3.02850	2.889E-03
74.00	1100.57	3.04162	2.881E-03

Table 18 (Contd.)

T(°C)	P(MM)	LOGP(MM)	1/T(K)
75.00	1134.11	3.05466	2.872E-03
76.00	1168.47	3.06762	2.864E-03
77.00	1203.64	3.08050	2.856E-03
78.00	1239.64	3.09330	2.848E-03
79.00	1276.49	3.10602	2.840E-03
80.00	1314.21	3.11866	2.832E-03
81.00	1352.79	3.13123	2.824E-03
82.00	1392.27	3.14372	2.816E-03
83.00	1432.65	3.15614	2.808E-03
84.00	1473.95	3.16848	2.800E-03
85.00	1516.18	3.18075	2.792E-03
86.00	1559.36	3.19295	2.784E-03
87.00	1603.49	3.20507	2.777E-03
88.00	1648.60	3.21712	2.769E-03
89.00	1694.70	3.22909	2.761E-03
90.00	1741.81	3.24100	2.754E-03
91.00	1789.93	3.25284	2.746E-03
92.00	1839.09	3.26460	2.739E-03
93.00	1889.30	3.27630	2.731E-03
94.00	1940.57	3.28793	2.724E-03
95.00	1992.92	3.29949	2.716E-03
96.00	2046.36	3.31098	2.709E-03
97.00	2100.91	3.32241	2.702E-03
98.00	2156.59	3.33377	2.694E-03
99.00	2213.40	3.34506	2.687E-03
100.00	2271.37	3.35629	2.680E-03

Table 19

VAPOR PRESSURES FOR PLUTONIUM HEXAFLUORIDE

T(C)	P(MM)	LOGP(MM)	1/T(K)
50.00	487.05	2.68758	3.095E-03
50.10	489.84	2.69005	3.094E-03
50.20	492.64	2.69253	3.093E-03
50.30	495.45	2.69500	3.092E-03
50.40	498.28	2.69747	3.091E-03
50.50	501.12	2.69994	3.090E-03
50.60	503.98	2.70241	3.089E-03
50.70	506.85	2.70488	3.088E-03
50.80	509.74	2.70734	3.087E-03
50.90	512.64	2.70981	3.086E-03
51.00	515.55	2.71227	3.085E-03
51.10	518.48	2.71473	3.084E-03
51.20	521.43	2.71720	3.083E-03
51.30	524.39	2.71965	3.082E-03
51.40	527.37	2.72211	3.081E-03
51.50	530.36	2.72457	3.080E-03
51.60	533.23	2.72692	3.079E-03
51.70	535.09	2.72843	3.078E-03
51.80	536.95	2.72993	3.077E-03
51.90	538.82	2.73144	3.076E-03
52.00	540.69	2.73295	3.076E-03
52.10	542.56	2.73445	3.075E-03
52.20	544.44	2.73595	3.074E-03
52.30	546.33	2.73745	3.073E-03
52.40	548.22	2.73896	3.072E-03
52.50	550.12	2.74046	3.071E-03
52.60	552.02	2.74196	3.070E-03
52.70	553.93	2.74345	3.069E-03

Table 19 (Contd.)

T (C)	P (MM)	LOGP (MM)	1/T (K)
52.80	555.84	2.74495	3.068E-03
52.90	557.76	2.74645	3.067E-03
53.00	559.68	2.74794	3.066E-03
53.10	561.61	2.74944	3.065E-03
53.20	563.55	2.75093	3.064E-03
53.30	565.49	2.75242	3.063E-03
53.40	567.43	2.75392	3.062E-03
53.50	569.38	2.75541	3.061E-03
53.60	571.34	2.75690	3.060E-03
53.70	573.30	2.75838	3.060E-03
53.80	575.27	2.75987	3.059E-03
53.90	577.24	2.76136	3.058E-03
54.00	579.22	2.76284	3.057E-03
54.10	581.20	2.76433	3.056E-03
54.20	583.19	2.76581	3.055E-03
54.30	585.19	2.76730	3.054E-03
54.40	587.19	2.76878	3.053E-03
54.50	589.19	2.77026	3.052E-03
54.60	591.20	2.77174	3.051E-03
54.70	593.22	2.77322	3.050E-03
54.80	595.24	2.77469	3.049E-03
54.90	597.27	2.77617	3.048E-03
55.00	599.30	2.77765	3.047E-03
55.10	601.34	2.77912	3.046E-03
55.20	603.39	2.78060	3.046E-03
55.30	605.44	2.78207	3.045E-03
55.40	607.49	2.78354	3.044E-03
55.50	609.56	2.78501	3.043E-03

Table 19 (Contd.)

T (C)	P (MM)	LOGP (MM)	1/T (K)
55.60	611.62	2.78648	3.042E-03
55.70	613.70	2.78795	3.041E-03
55.80	615.77	2.78942	3.040E-03
55.90	617.86	2.79089	3.039E-03
56.00	619.95	2.79235	3.038E-03
56.10	622.04	2.79382	3.037E-03
56.20	624.14	2.79528	3.036E-03
56.30	626.25	2.79675	3.035E-03
56.40	628.36	2.79821	3.034E-03
56.50	630.48	2.79967	3.034E-03
56.60	632.61	2.80113	3.033E-03
56.70	634.74	2.80259	3.032E-03
56.80	636.87	2.80405	3.031E-03
56.90	639.01	2.80551	3.030E-03
57.00	641.16	2.80697	3.029E-03
57.10	643.31	2.80842	3.028E-03
57.20	645.47	2.80988	3.027E-03
57.30	647.64	2.81133	3.026E-03
57.40	649.81	2.81279	3.025E-03
57.50	651.98	2.81424	3.024E-03
57.60	654.17	2.81569	3.023E-03
57.70	656.36	2.81714	3.023E-03
57.80	658.55	2.81859	3.022E-03
57.90	660.75	2.82004	3.021E-03
58.00	662.96	2.82148	3.020E-03
58.10	665.17	2.82293	3.019E-03
58.20	667.39	2.82438	3.018E-03
58.30	669.61	2.82582	3.017E-03

Table 19 (Contd.)

T (C)	P (MM)	LOGP (MM)	1/T (K)
58.40	671.84	2.82727	3.016E-03
58.50	674.08	2.82871	3.015E-03
58.60	676.32	2.83015	3.014E-03
58.70	678.56	2.83159	3.013E-03
58.80	680.82	2.83303	3.013E-03
58.90	683.08	2.83447	3.012E-03
59.00	685.34	2.83591	3.011E-03
59.10	687.62	2.83735	3.010E-03
59.20	689.89	2.83878	3.009E-03
59.30	692.18	2.84022	3.008E-03
59.40	694.47	2.84165	3.007E-03
59.50	696.77	2.84309	3.006E-03
59.60	699.07	2.84452	3.005E-03
59.70	701.38	2.84595	3.004E-03
59.80	703.69	2.84738	3.003E-03
59.90	706.01	2.84881	3.003E-03
60.00	708.34	2.85024	3.002E-03
60.10	710.67	2.85167	3.001E-03
60.20	713.01	2.85310	3.000E-03
60.30	715.36	2.85452	2.999E-03
60.40	717.71	2.85595	2.998E-03
60.50	720.07	2.85737	2.997E-03
60.60	722.43	2.85880	2.996E-03
60.70	724.80	2.86022	2.995E-03
60.80	727.18	2.86164	2.994E-03
60.90	729.56	2.86306	2.994E-03
61.00	731.95	2.86448	2.993E-03
61.10	734.34	2.86590	2.992E-03

Table 19 (Contd.)

T(C)	P(MM)	LOGP(MM)	1/T(K)
61.20	736.75	2.86732	2.991E-03
61.30	739.15	2.86873	2.990E-03
61.40	741.57	2.87015	2.989E-03
61.50	743.99	2.87157	2.988E-03
61.60	746.42	2.87298	2.987E-03
61.70	748.85	2.87439	2.986E-03
61.80	751.29	2.87581	2.986E-03
61.90	753.74	2.87722	2.985E-03
62.00	756.19	2.87863	2.984E-03
62.10	758.65	2.88004	2.983E-03
62.20	761.11	2.88145	2.982E-03
62.30	763.58	2.88286	2.981E-03
62.40	766.06	2.88426	2.980E-03
62.50	768.55	2.88567	2.979E-03
62.60	771.04	2.88708	2.978E-03
62.70	773.54	2.88848	2.978E-03
62.80	776.04	2.88988	2.977E-03
62.90	778.55	2.89129	2.976E-03
63.00	781.07	2.89269	2.975E-03
63.10	783.59	2.89409	2.974E-03
63.20	786.12	2.89549	2.973E-03
63.30	788.66	2.89689	2.972E-03
63.40	791.20	2.89829	2.971E-03
63.50	793.75	2.89968	2.970E-03
63.60	796.31	2.90108	2.970E-03
63.70	798.87	2.90248	2.969E-03
63.80	801.44	2.90387	2.968E-03
63.90	804.02	2.90527	2.967E-03

Table 19 (Contd.)

T (C)	P (MM)	LOGP (MM)	1/T (K)
64.00	806.60	2.90666	2.966E-03
64.10	809.19	2.90805	2.965E-03
64.20	811.79	2.90944	2.964E-03
64.30	814.39	2.91083	2.963E-03
64.40	817.00	2.91222	2.963E-03
64.50	819.61	2.91361	2.962E-03
64.60	822.24	2.91500	2.961E-03
64.70	824.87	2.91638	2.960E-03
64.80	827.50	2.91777	2.959E-03
64.90	830.15	2.91916	2.958E-03
65.00	832.80	2.92054	2.957E-03
65.10	835.45	2.92192	2.956E-03
65.20	838.12	2.92331	2.956E-03
65.30	840.79	2.92469	2.955E-03
65.40	843.47	2.92607	2.954E-03
65.50	846.15	2.92745	2.953E-03
65.60	848.84	2.92883	2.952E-03
65.70	851.54	2.93020	2.951E-03
65.80	854.24	2.93158	2.950E-03
65.90	856.95	2.93296	2.949E-03
66.00	859.67	2.93433	2.949E-03
66.10	862.40	2.93571	2.948E-03
66.20	865.13	2.93708	2.947E-03
66.30	867.87	2.93845	2.946E-03
66.40	870.61	2.93983	2.945E-03
66.50	873.37	2.94120	2.944E-03
66.60	876.13	2.94257	2.943E-03
66.70	878.89	2.94394	2.942E-03

Table 19 (Contd.)

T (C)	P (MM)	LOGP (MM)	1/T (K)
66.80	881.67	2.94530	2.942E-03
66.90	884.45	2.94667	2.941E-03
67.00	887.24	2.94804	2.940E-03
67.10	890.03	2.94941	2.939E-03
67.20	892.83	2.95077	2.938E-03
67.30	895.64	2.95213	2.937E-03
67.40	898.46	2.95350	2.936E-03
67.50	901.28	2.95486	2.936E-03
67.60	904.11	2.95622	2.935E-03
67.70	906.95	2.95758	2.934E-03
67.80	909.79	2.95894	2.933E-03
67.90	912.64	2.96030	2.932E-03
68.00	915.50	2.96166	2.931E-03
68.10	918.37	2.96302	2.930E-03
68.20	921.24	2.96437	2.930E-03
68.30	924.12	2.96573	2.929E-03
68.40	927.01	2.96708	2.928E-03
68.50	929.90	2.96844	2.927E-03
68.60	932.81	2.96979	2.926E-03
68.70	935.71	2.97114	2.925E-03
68.80	938.63	2.97249	2.924E-03
68.90	941.55	2.97385	2.924E-03
69.00	944.48	2.97520	2.923E-03
69.10	947.42	2.97654	2.922E-03
69.20	950.37	2.97789	2.921E-03
69.30	953.32	2.97924	2.920E-03
69.40	956.28	2.98059	2.919E-03
69.50	959.25	2.98193	2.918E-03

Table 19 (Contd.)

T (C)	P (MM)	LOGP (MM)	1/T (K)
69.60	962.22	2.98328	2.918E-03
69.70	965.20	2.98462	2.917E-03
69.80	968.19	2.98596	2.916E-03
69.90	971.19	2.98730	2.915E-03
70.00	974.19	2.98865	2.914E-03
70.10	977.21	2.98999	2.913E-03
70.20	980.22	2.99133	2.912E-03
70.30	983.25	2.99266	2.912E-03
70.40	986.28	2.99400	2.911E-03
70.50	989.33	2.99534	2.910E-03
70.60	992.37	2.99668	2.909E-03
70.70	995.43	2.99801	2.908E-03
70.80	998.49	2.99935	2.907E-03
70.90	1001.57	3.00068	2.907E-03
71.00	1004.64	3.00201	2.906E-03
71.10	1007.73	3.00334	2.905E-03
71.20	1010.82	3.00468	2.904E-03
71.30	1013.93	3.00601	2.903E-03
71.40	1017.03	3.00734	2.902E-03
71.50	1020.15	3.00866	2.901E-03
71.60	1023.28	3.00999	2.901E-03
71.70	1026.41	3.01132	2.900E-03
71.80	1029.55	3.01265	2.899E-03
71.90	1032.69	3.01397	2.898E-03
72.00	1035.85	3.01530	2.897E-03
72.10	1039.01	3.01662	2.896E-03
72.20	1042.18	3.01794	2.896E-03
72.30	1045.36	3.01927	2.895E-03

Table 19 (Contd.)

T(C)	P(MM)	LOGP(MM)	1/T(K)
72.40	1048.54	3.02059	2.894E-03
72.50	1051.74	3.02191	2.893E-03
72.60	1054.94	3.02323	2.892E-03
72.70	1058.15	3.02455	2.891E-03
72.80	1061.36	3.02586	2.891E-03
72.90	1064.59	3.02718	2.890E-03
73.00	1067.82	3.02850	2.889E-03
73.10	1071.06	3.02981	2.888E-03
73.20	1074.31	3.03113	2.887E-03
73.30	1077.56	3.03244	2.886E-03
73.40	1080.82	3.03376	2.886E-03
73.50	1084.10	3.03507	2.885E-03
73.60	1087.37	3.03638	2.884E-03
73.70	1090.66	3.03769	2.883E-03
73.80	1093.96	3.03900	2.882E-03
73.90	1097.26	3.04031	2.881E-03
74.00	1100.57	3.04162	2.881E-03
74.10	1103.89	3.04292	2.880E-03
74.20	1107.21	3.04423	2.879E-03
74.30	1110.55	3.04554	2.878E-03
74.40	1113.89	3.04684	2.877E-03
74.50	1117.24	3.04815	2.876E-03
74.60	1120.60	3.04945	2.876E-03
74.70	1123.97	3.05075	2.875E-03
74.80	1127.34	3.05205	2.874E-03
74.90	1130.72	3.05336	2.873E-03
75.00	1134.11	3.05466	2.872E-03
75.10	1137.51	3.05596	2.872E-03

Table 19 (Contd.)

T(C)	P(MM)	LOGP(MM)	1/T(K)
75.20	1140.92	3.05725	2.871E-03
75.30	1144.33	3.05855	2.870E-03
75.40	1147.75	3.05985	2.869E-03
75.50	1151.19	3.06115	2.868E-03
75.60	1154.62	3.06244	2.867E-03
75.70	1158.07	3.06374	2.867E-03
75.80	1161.53	3.06503	2.866E-03
75.90	1164.99	3.06632	2.865E-03
76.00	1168.46	3.06761	2.864E-03
76.10	1171.94	3.06891	2.863E-03
76.20	1175.43	3.07020	2.862E-03
76.30	1178.93	3.07149	2.862E-03
76.40	1182.43	3.07278	2.861E-03
76.50	1185.94	3.07406	2.860E-03
76.60	1189.47	3.07535	2.859E-03
76.70	1193.00	3.07664	2.858E-03
76.80	1196.53	3.07792	2.858E-03
76.90	1200.08	3.07921	2.857E-03
77.00	1203.63	3.08049	2.856E-03
77.10	1207.20	3.08178	2.855E-03
77.20	1210.77	3.08306	2.854E-03
77.30	1214.35	3.08434	2.853E-03
77.40	1217.93	3.08562	2.853E-03
77.50	1221.53	3.08690	2.852E-03
77.60	1225.13	3.08818	2.851E-03
77.70	1228.75	3.08946	2.850E-03
77.80	1232.37	3.09074	2.849E-03
77.90	1236.00	3.09202	2.849E-03

Table 19 (Contd.)

T (C)	P (MM)	LOGP (MM)	1/T (K)
78.00	1239.64	3.09329	2.848E-03
78.10	1243.28	3.09457	2.847E-03
78.20	1246.94	3.09585	2.846E-03
78.30	1250.60	3.09712	2.845E-03
78.40	1254.28	3.09839	2.845E-03
78.50	1257.96	3.09967	2.844E-03
78.60	1261.65	3.10094	2.843E-03
78.70	1265.34	3.10221	2.842E-03
78.80	1269.05	3.10348	2.841E-03
78.90	1272.76	3.10475	2.841E-03
79.00	1276.49	3.10602	2.840E-03
79.10	1280.22	3.10729	2.839E-03
79.20	1283.96	3.10855	2.838E-03
79.30	1287.71	3.10982	2.837E-03
79.40	1291.47	3.11108	2.836E-03
79.50	1295.24	3.11235	2.836E-03
79.60	1299.01	3.11361	2.835E-03
79.70	1302.80	3.11488	2.834E-03
79.80	1306.59	3.11614	2.833E-03
79.90	1310.39	3.11740	2.832E-03
80.00	1314.20	3.11866	2.832E-03
80.10	1318.02	3.11992	2.831E-03
80.20	1321.85	3.12118	2.830E-03
80.30	1325.69	3.12244	2.829E-03
80.40	1329.53	3.12370	2.828E-03
80.50	1333.39	3.12496	2.828E-03
80.60	1337.25	3.12621	2.827E-03
80.70	1341.12	3.12747	2.826E-03

Table 19 (Contd.)

T(C)	P(MM)	LOGP(MM)	1/T(K)
80.80	1345.00	3.12872	2.825E-03
80.90	1348.89	3.12998	2.824E-03
81.00	1352.79	3.13123	2.824E-03
81.10	1356.70	3.13248	2.823E-03
81.20	1360.61	3.13373	2.822E-03
81.30	1364.54	3.13499	2.821E-03
81.40	1368.47	3.13624	2.820E-03
81.50	1372.42	3.13749	2.820E-03
81.60	1376.37	3.13873	2.819E-03
81.70	1380.33	3.13998	2.818E-03
81.80	1384.30	3.14123	2.817E-03
81.90	1388.28	3.14248	2.817E-03
82.00	1392.27	3.14372	2.816E-03
82.10	1396.26	3.14497	2.815E-03
82.20	1400.27	3.14621	2.814E-03
82.30	1404.29	3.14746	2.813E-03
82.40	1408.31	3.14870	2.813E-03
82.50	1412.34	3.14994	2.812E-03
82.60	1416.39	3.15118	2.811E-03
82.70	1420.44	3.15242	2.810E-03
82.80	1424.50	3.15366	2.809E-03
82.90	1428.57	3.15490	2.809E-03
83.00	1432.65	3.15614	2.808E-03
83.10	1436.74	3.15738	2.807E-03
83.20	1440.83	3.15861	2.806E-03
83.30	1444.94	3.15985	2.805E-03
83.40	1449.06	3.16109	2.805E-03
83.50	1453.18	3.16232	2.804E-03

Table 19 (Contd.)

T(C)	P(MM)	LOGP(MM)	1/T(K)
83.60	1457.31	3.16355	2.803E-03
83.70	1461.46	3.16479	2.802E-03
83.80	1465.61	3.16602	2.802E-03
83.90	1469.77	3.16725	2.801E-03
84.00	1473.94	3.16848	2.800E-03
84.10	1478.13	3.16971	2.799E-03
84.20	1482.32	3.17094	2.798E-03
84.30	1486.51	3.17217	2.798E-03
84.40	1490.72	3.17340	2.797E-03
84.50	1494.94	3.17462	2.796E-03
84.60	1499.17	3.17585	2.795E-03
84.70	1503.41	3.17708	2.794E-03
84.80	1507.65	3.17830	2.794E-03
84.90	1511.91	3.17953	2.793E-03
85.00	1516.17	3.18075	2.792E-03
85.10	1520.45	3.18197	2.791E-03
85.20	1524.73	3.18319	2.791E-03
85.30	1529.03	3.18442	2.790E-03
85.40	1533.33	3.18564	2.789E-03
85.50	1537.64	3.18686	2.788E-03
85.60	1541.96	3.18807	2.787E-03
85.70	1546.30	3.18929	2.787E-03
85.80	1550.64	3.19051	2.786E-03
85.90	1554.99	3.19173	2.785E-03
86.00	1559.35	3.19294	2.784E-03
86.10	1563.72	3.19416	2.784E-03
86.20	1568.10	3.19537	2.783E-03
86.30	1572.49	3.19659	2.782E-03

Table 19 (Contd.)

T(C)	P(MM)	LOGP(MM)	1/T(K)
86.40	1576.89	3.19780	2.781E-03
86.50	1581.30	3.19901	2.780E-03
86.60	1585.71	3.20023	2.780E-03
86.70	1590.14	3.20144	2.779E-03
86.80	1594.58	3.20265	2.778E-03
86.90	1599.03	3.20386	2.777E-03
87.00	1603.49	3.20507	2.777E-03
87.10	1607.95	3.20627	2.776E-03
87.20	1612.43	3.20748	2.775E-03
87.30	1616.92	3.20869	2.774E-03
87.40	1621.41	3.20989	2.774E-03
87.50	1625.92	3.21110	2.773E-03
87.60	1630.43	3.21230	2.772E-03
87.70	1634.96	3.21351	2.771E-03
87.80	1639.49	3.21471	2.770E-03
87.90	1644.04	3.21591	2.770E-03
88.00	1648.60	3.21711	2.769E-03
88.10	1653.16	3.21832	2.768E-03
88.20	1657.74	3.21952	2.767E-03
88.30	1662.32	3.22072	2.767E-03
88.40	1666.92	3.22191	2.766E-03
88.50	1671.52	3.22311	2.765E-03
88.60	1676.14	3.22431	2.764E-03
88.70	1680.76	3.22551	2.764E-03
88.80	1685.40	3.22670	2.763E-03
88.90	1690.04	3.22790	2.762E-03
89.00	1694.70	3.22909	2.761E-03
89.10	1699.36	3.23029	2.761E-03

Table 19 (Contd.)

T (C)	P (MM)	LOGP (MM)	1/T (K)
89.20	1704.04	3.23148	2.760E-03
89.30	1708.72	3.23267	2.759E-03
89.40	1713.42	3.23386	2.758E-03
89.50	1718.12	3.23505	2.757E-03
89.60	1722.84	3.23624	2.757E-03
89.70	1727.56	3.23743	2.756E-03
89.80	1732.30	3.23862	2.755E-03
89.90	1737.04	3.23981	2.754E-03
90.00	1741.80	3.24100	2.754E-03
90.10	1746.57	3.24219	2.753E-03
90.20	1751.34	3.24337	2.752E-03
90.30	1756.13	3.24456	2.751E-03
90.40	1760.93	3.24574	2.751E-03
90.50	1765.73	3.24693	2.750E-03
90.60	1770.55	3.24811	2.749E-03
90.70	1775.38	3.24929	2.748E-03
90.80	1780.22	3.25047	2.748E-03
90.90	1785.07	3.25165	2.747E-03
91.00	1789.92	3.25283	2.746E-03
91.10	1794.79	3.25401	2.745E-03
91.20	1799.67	3.25519	2.745E-03
91.30	1804.56	3.25637	2.744E-03
91.40	1809.46	3.25755	2.743E-03
91.50	1814.37	3.25873	2.742E-03
91.60	1819.29	3.25990	2.742E-03
91.70	1824.23	3.26108	2.741E-03
91.80	1829.17	3.26225	2.740E-03
91.90	1834.12	3.26343	2.739E-03

Table 19 (Contd.)

T(C)	P(MM)	LOGP(MM)	1/T(K)
92.00	1839.08	3.26460	2.739E-03
92.10	1844.05	3.26577	2.738E-03
92.20	1849.04	3.26695	2.737E-03
92.30	1854.03	3.26812	2.736E-03
92.40	1859.04	3.26929	2.736E-03
92.50	1864.05	3.27046	2.735E-03
92.60	1869.08	3.27163	2.734E-03
92.70	1874.11	3.27280	2.733E-03
92.80	1879.16	3.27396	2.733E-03
92.90	1884.22	3.27513	2.732E-03
93.00	1889.29	3.27630	2.731E-03
93.10	1894.37	3.27746	2.730E-03
93.20	1899.46	3.27863	2.730E-03
93.30	1904.56	3.27979	2.729E-03
93.40	1909.67	3.28096	2.728E-03
93.50	1914.79	3.28212	2.727E-03
93.60	1919.92	3.28328	2.727E-03
93.70	1925.06	3.28445	2.726E-03
93.80	1930.22	3.28561	2.725E-03
93.90	1935.38	3.28677	2.724E-03
94.00	1940.56	3.28793	2.724E-03
94.10	1945.74	3.28909	2.723E-03
94.20	1950.94	3.29024	2.722E-03
94.30	1956.15	3.29140	2.721E-03
94.40	1961.37	3.29256	2.721E-03
94.50	1966.60	3.29372	2.720E-03
94.60	1971.84	3.29487	2.719E-03
94.70	1977.09	3.29603	2.719E-03

Table 19 (Contd.)

T(C)	P(MM)	LOGP(MM)	1/T(K)
94.80	1982.35	3.29718	2.718E-03
94.90	1987.62	3.29833	2.717E-03
95.00	1992.91	3.29949	2.716E-03
95.10	1998.20	3.30064	2.716E-03
95.20	2003.51	3.30179	2.715E-03
95.30	2008.82	3.30294	2.714E-03
95.40	2014.15	3.30409	2.713E-03
95.50	2019.49	3.30524	2.713E-03
95.60	2024.84	3.30639	2.712E-03
95.70	2030.20	3.30754	2.711E-03
95.80	2035.57	3.30869	2.710E-03
95.90	2040.95	3.30983	2.710E-03
96.00	2046.35	3.31098	2.709E-03
96.10	2051.75	3.31213	2.708E-03
96.20	2057.17	3.31327	2.707E-03
96.30	2062.60	3.31441	2.707E-03
96.40	2068.03	3.31556	2.706E-03
96.50	2073.48	3.31670	2.705E-03
96.60	2078.94	3.31784	2.705E-03
96.70	2084.42	3.31898	2.704E-03
96.80	2089.90	3.32013	2.703E-03
96.90	2095.39	3.32127	2.702E-03
97.00	2100.90	3.32241	2.702E-03
97.10	2106.42	3.32354	2.701E-03
97.20	2111.94	3.32468	2.700E-03
97.30	2117.48	3.32582	2.699E-03
97.40	2123.03	3.32696	2.699E-03
97.50	2128.60	3.32809	2.698E-03

Table 19 (Contd.)

T(C)	P(MM)	LOGP(MM)	1/T(K)
97.60	2134.17	3.32923	2.697E-03
97.70	2139.75	3.33036	2.697E-03
97.80	2145.35	3.33150	2.696E-03
97.90	2150.96	3.33263	2.695E-03
98.00	2156.58	3.33376	2.694E-03
98.10	2162.20	3.33490	2.694E-03
98.20	2167.85	3.33603	2.693E-03
98.30	2173.50	3.33716	2.692E-03
98.40	2179.16	3.33829	2.691E-03
98.50	2184.84	3.33942	2.691E-03
98.60	2190.53	3.34055	2.690E-03
98.70	2196.23	3.34168	2.689E-03
98.80	2201.94	3.34280	2.689E-03
98.90	2207.66	3.34393	2.688E-03
99.00	2213.39	3.34506	2.687E-03
99.10	2219.14	3.34618	2.686E-03
99.20	2224.89	3.34731	2.686E-03
99.30	2230.66	3.34843	2.685E-03
99.40	2236.44	3.34956	2.684E-03
99.50	2242.23	3.35068	2.683E-03
99.60	2248.03	3.35180	2.683E-03
99.70	2253.85	3.35292	2.682E-03
99.80	2259.67	3.35405	2.681E-03
99.90	2265.51	3.35517	2.681E-03
100.00	2271.36	3.35629	2.680E-03

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